Chemical Engineering Report Series
Kemian laitetekniikan raporttisarja No. 52
Espoo 2007

MODELLING AND MEASURING VAPOUR-LIQUID EQUILIBRIA FOR THE REMOVAL OF SULPHUR COMPOUNDS

Erlin Sapei

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission for public examination and debate in Auditorium Ke 2 at Helsinki University of Technology (Espoo, Finland) on the 9th of November, 2007, at 12 o'clock.

Helsinki University of Technology
Department of Chemical Technology
Laboratory of Chemical Engineering and Plant Design

Teknillinen korkeakoulu
Kemian tekniikan osasto
Kemian laitetekniikan ja tehdassuunnittelun laboratorio

Distribution:
Helsinki University of Technology
Laboratory of Chemical Engineering and Plant Design
P. O. Box 6100
FI-02015 TKK
Tel. + 358-9-451 2634
Fax. +358-9-451 2694
E-mail: sapei@cc.hut.fi

ISBN 978-951-22-8998-1
ISSN 1236-875X

Multiprint Oy
Espoo 2007

ABSTRACT

Increasing concern about air pollution has led many countries to adopt more stringent regulations, which impose an ultra-low concentration of sulphur in gasoline. These regulations place many challenges for the refining industry. Lower sulphur levels are being recommended for gasoline and diesel for environmental reasons.

New methods and innovations are required to further reduce the sulphur level in liquid fuels. Separation process design to accomplish the removal of sulphur compounds requires knowledge of the vapour-liquid equilibrium (VLE) of sulphur compounds with hydrocarbons, particularly their activity coefficients at infinite dilution. However, the investigations concerning the systems containing sulphur compounds are very limited.

This thesis deals with the VLE measurements of selected sulphur compounds (1-propanethiol, diethyl sulphide, and thiophene) with various hydrocarbons (C_6 to C_8) and 2-ethoxy-2-methylpropane (ETBE) under isobaric and isothermal conditions, using a circulation still and the infinite dilutions activity coefficients measurements of 1-propanethiol, ethyl methyl sulphide, and thiophene in toluene, *n*-heptane, and 2,2,4-trimethylpentane at 90 kPa using comparative ebulliometer techniques.

The gamma-phi approach was used in the calculation of VLE. The activity coefficients of the liquid phase (γ) were correlated with the Wilson model. The Wilson model gave a good correlation for all systems. The activity coefficients at infinite dilution (γ^{∞}) were extrapolated from the VLE measurements with the Wilson model.

The γ^{∞} values of sulphur compounds for the systems thiophene + toluene and thiophene + 2,2,4-trimethylpentane obtained from the recirculation still measurements are compared with the γ^{∞} values of sulphur compounds obtained from the comparative ebulliometer measurements. The agreement between the measurements is good.

All the measured γ^{∞} of sulphur compounds in hydrocarbons are less than two. 1-Propanethiol, thiophene, and diethyl sulphide in toluene show nearly ideal behaviour, and thus the γ^{∞} of sulphur compounds for these systems are one. The activity coefficients of sulphur compounds in hydrocarbons show the typical behaviour of positive deviations from Raoult's law, which become smaller with increasing temperature and with an increase in the number of C-atoms of the alkanes.

The systems 1-propanethiol, thiophene, and diethyl sulphide in toluene show nearly ideal behaviour. No azeotrope formation was observed for the systems thiophene + 1-hexene and diethyl sulphide + 1-hexene. The reaction between 1-propanethiol and 1-hexene was observed. The systems thiophene + *n*-hexane and thiophene + 2,2,4-trimethylpentane, as well as the systems diethyl sulphide + *n*-heptane and diethyl sulphide + 2,2,4-trimethylpentane, show positive deviations from Raoult's law. These systems exhibit maximum pressure azeotropy. The systems thiophene + 1-hexene and thiophene + 2-ethoxy-2-methylpropane, as well as the systems diethyl sulphide with *n*-hexane, 1-hexene, cyclohexane, and 2-ethoxy-2-methylpropane, show positive deviation and strong nonideality. No azeotropes formed in these systems.

The original UNIFAC predictive model is adequate to describe the behaviour of sulphur in hydrocarbons, even though its application is limited to the availability of the functional group interaction parameters. COSMO-RS gives poor prediction for all the systems studied, and thus it is not currently a suitable model for predicting the behaviour of systems containing sulphur compounds.

These new consistent measurements can be used to improve and develop thermodynamic models in dilute systems, and thus the behaviour of organic sulphur compounds in the distillation of hydrocarbons can be simulated.

PREFACE

This work was carried out between 2004 and 2007 in the Laboratory of Chemical Engineering and Plant Design at Helsinki University of Technology, Finland. The financial support of Neste Oil Oyj, Neste Jacobs Oy, TEKES (the Finnish Funding Agency for Technology and Innovation), and the Fortum Foundation is gratefully acknowledged.

I would like to express my deepest gratitude to my supervisor, Professor Juhani Aittamaa, whose insight, enthusiasm, and ability to see both the finer details and the bigger picture has been invaluable during the work on this thesis. He has always taken an active interest in my work, and I am proud to have been given the opportunity to work under his supervision. Without his support and contributions, this thesis would never have emerged.

I am also grateful to my co-supervisor D.Sc Kari I. Keskinen for his valuable contributions to this research work. His deep knowledge of thermodynamics, inspiring discussions, and valuable detailed comments on the manuscript has contributed significantly to this thesis.

I would like to thank Prof. Emer. Simo Liukkonen, who supervised the thermodynamic courses of my graduate studies. Our discussions have been very useful in providing a strong theoretical background in thermodynamics.

I wish to acknowledge all of the co-authors for their significant contributions to this thesis. In particular I owe my sincere thanks to Dr. Petri Uusi-Kyyny. He has always been willing to provide help or discuss parts of my work. My discussions with him have been especially helpful, because of his expertise and understanding of thermodynamic and experimental work. His constant constructive criticism of my work has had a great impact on the quality of the results presented in this thesis. I want to thank to Dr. Kim Younghun, who was very helpful at the beginning of my experimental work. His systematic way of working has been an inspiration for me. His constant encouragement, not only on a scientific but also on a personal level, is gratefully appreciated. Ms. Anna Zaytseva is acknowledged for her valuable contribution to the COSMO-RS calculations.

I am indebted to Dr. Juha-Pekka Pokki for his remarkable help in helping me get started with the VLEFIT program, and for numerous interesting discussions on these topics. Ms. Piia Haimi is acknowledged for her help and support with the gas chromatograph. Ms. Hanne Koskiniemi deserves many thanks for her measurement assistance.

My special thanks to Kalevi Karppinen, the technician in the glass-blowing workshop at Helsinki University of Technology (now retired), for his patience and readiness in repairing the broken glass equipment.

Furthermore, I would like to thank all of my colleagues at the Chemical Engineering and Plant Design Laboratory for an innovative and pleasant working environment. I have to especially thank Claudia Dell'Era and Helena Laavi for their help, for all our discussions, and for being good friends. I would also like to thank Sirpa Aaltonen and Lasse Westerlund for their help with administrative issues.

Finally, I would like to express my gratitude to my parents, sisters, and brothers for their unconditional support and encouragement. My warmest thanks go to my husband, Wong

Jauw Seng for his endless love, support, patience and understanding during all these demanding years. This thesis would not have been possible without him. I would like to dedicate this thesis to all of them.

Espoo, November 2007
Erlin Sapei

LIST OF PUBLICATIONS

This thesis is based on the following eight publications, which are referred to in the text by the Roman numerals I-VIII.

[I] Kim, Younghun, Sapei, E., Keskinen, K. I., Aittamaa, J., Vapor-liquid equilibrium for binary systems of 2-propanol + 1,1-diethoxyethane at 353 K, ethyl ethanoate + 1,1-diethoxyethane at 348 K, and 2-propanone + 1,1-diethoxyethane at 328 K, *J. Chem. Eng. Data*, **50** (2005) 364-368.

[II] 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*, **51** (2006) 1372-1376.

[III] Sapei, E., Zaytseva, A., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J., 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, *J. Chem. Eng. Data*, **51** (2006) 2203-2208.

[IV] Sapei, E., Zaytseva, A., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J., 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, *J. Chem. Eng. Data*, **52** (2007) 192-198.

[V] Sapei, E., Zaytseva, A., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J., 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, *J. Chem. Eng. Data*, **52** (2007) 571-576.

[VI] Sapei, E., Zaytseva, A., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J., Vapor-liquid equilibrium for binary system of diethyl sulfide + cyclohexane at (353.15 and 343.15) K and diethyl sulfide + 2-ethoxy-2-methylpropane at (343.15 and 333.15) K, *Fluid Phase Equilib*., **252** (2007) 130-136.

[VII] Sapei, E., Zaytseva, A., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J., Vapor-liquid equilibrium for binary system of thiophene + 2,2,4-trimethylpentane at (353.15 and 343.15) K and thiophene + 2-ethoxy-2-methylpropane at (343.15 and 333.15) K, *Fluid Phase Equilib*., accepted for publication on 15.06.2007. To be published in 2007.

[VIII] Sapei, E., Uusi-Kyyny, P., Keskinen, K. I., Aittamaa, J. Infinite dilution activity coefficients of organic sulphur compounds in hydrocarbons by comparative ebulliometry. World Congress of Chemical Engineering, 7th, Glasgow, United Kingdom, 2005, 83582/1-83582/6.

THE AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

[I] This article is part of an effort to find accurate vapour-liquid equilibrium (VLE) data for a process using or producing ethanol. The components investigated are possible ethanol impurities when ethanol is produced by fermentation followed by distillation and adsorption. The author carried out the measurements together with Kim Younghun and contributed to the preparation of the manuscript.

[II] This article considers isobaric VLE for three systems with three different organic sulphur compounds (1-propanethiol, thiophene, and diethyl sulphide) with toluene. The author made the measurements, performed the calculations, and wrote the manuscript.

[III] Isothermal VLE were carried out for thiophene with *n*-hexane and 1-hexene. Another sampling analysis method using a refractometer was tested. The author made the measurements, performed the calculations, and wrote the manuscript.

[IV] Isothermal VLE were carried out for diethyl sulphide with *n*-heptane and 2,2,4-trimethylpentane. The measured diethyl sulphide + *n*-heptane VLE were used simultaneously with the excess enthalpy from the literature for a correlation of temperature-dependent Wilson parameters. The author made the measurements, performed the calculations and wrote the manuscript.

[V] Isothermal VLE were carried out for diethyl sulphide with *n*-hexane and 1-hexene. The measured diethyl sulphide + *n*-hexane VLE were used simultaneously with the excess enthalpy from the literature for a correlation of temperature-dependent Wilson parameters, and thus the new correlation gave the temperature dependence of the activity coefficient over a broader range. The author conducted part of the experiments, trained the technical staff in the operating procedures of the apparatus, performed the calculations, and wrote the manuscript.

[VI] Isothermal VLE were carried out for diethyl sulphide with cyclohexane and 2-ethoxy-2-methylpropane. The measured diethyl sulphide + cyclohexane VLE were used simultaneously with the excess enthalpy from the literature. The author performed the calculations and wrote the manuscript with the experimental assistance of Hanne Koskiniemi.

[VII] Isothermal VLE were carried out for thiophene with 2,2,4-trimethylpentane and 2-ethoxy-2-methylpropane. The author performed the calculations and wrote the manuscript with the experimental assistance of Hanne Koskiniemi.

[VIII] Infinite dilution activity coefficients of thiophene, 1-propanethiol, and ethyl methyl sulphide in toluene, *n*-heptane, and 2,2,4-trimethylpentane were measured with comparative ebulliometry at 90 kPa. The author built the apparatus together with the co-author Petri Uusi-Kyyny, tested the system, conducted the experiments, performed the calculations, and wrote the manuscript.

TABLE OF CONTENTS

ABSTRACT I

PREFACE III

LIST OF PUBLICATIONS V

THE AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS VI

TABLE OF CONTENTS VII

NOTATION IX

1 INTRODUCTION 1
1.1 Sulphur Compounds in Fuels 1
1.2 Environmental Issues 2
1.3 Removal of Sulphur Compounds 3
1.4 Systems of Interest 3

2 THERMODYNAMIC PRINCIPLES 6
2.1 Vapour-Liquid Equilibrium Concept 6
2.1.1 Vapour fugacity 6
2.1.2 Liquid fugacity 7
2.2 Correlation of Liquid Phase Activity Coefficient 8
2.3 Excess Enthalpy 9
2.4 Parameter Fitting and Objective Function 11
2.5 Differential Ebulliometry 12

3 PREDICTION OF LOW PRESSURE VAPOUR-LIQUID EQUILIBRIUM 14
3.1 UNIFAC (UNIQUAC Functional Group Activity Coefficient) 14
3.2 COSMO-RS (Conductor-like Screening Model for Real Solvents) 15

4 EXPERIMENTAL SETUP AND PROCEDURES 18
4.1 Circulation Still VLE Measurements 18
4.1.1 Experimental setup 18
4.1.2 Experimental procedures 19
4.1.2.1 Purity determination 19
4.1.2.2 VLE measurements 19
4.1.2.3 Analysis of VLE 19
4.1.2.3.1 Gas chromatography 19
4.1.2.3.2 Refractometry 20
4.1.2.4 Consistency tests 20
4.1.2.4.1 Area test 20
4.1.2.4.2 Infinite dilution test 20
4.1.2.4.3 Point test 21

4.2 Comparative Ebulliometry γ_i^{∞} Measurements 21
4.2.1 Experimental setup 21
4.2.2 Experimental procedures 22

5 RESULTS AND DISCUSSIONS 23
5.1 Recirculation Still 23
5.1.1 Wilson interaction parameters 23
5.1.2 Thermodynamic consistency tests 25
5.1.3 γ^{∞} of sulphur compounds in hydrocarbons 27
5.1.4 Azeotropy and ideality 31
5.1.5 Estimation methods 32
5.2 Differential Ebulliometry 42
5.2.1 Systems tested 42
5.2.2 Sulphur component-hydrocarbon mixtures 42

6 CONCLUSIONS 46

REFERENCES 48

APPENDIX I 51

NOTATION

a, b	attraction and co-volume parameters of SRK EOS
A, B	derived parameter of Soave-Redlich-Kwong (SRK) EOS
A_1, A_2	areas of GC peak
B_{ij}, B_{ii}, B_{jj}	second virial coefficient
D	criterion of area test
f	evaporation factor
f_i^{L}	fugacities of component i in the liquid phase, MPa
f_i^{S}	standard state fugacity, MPa
f_i^{V}	fugacities of component i in the vapour phase, MPa
F_2	gas chromatography response factor of component 2
G^{E}	excess Gibbs energy, $\mathrm{J\cdot mol^{-1}}$
H^{E}	molar excess enthalpy, $\mathrm{J\cdot mol^{-1}}$
I_1, I_2	criterion of infinite dilution test
k_{ij}	binary interaction parameters of SRK EOS
K_i	equilibrium constant of component i
m_1, m_2	masses of calibration sample in the gravimetrically prepared, g
M_1, M_2	molar masses, $\mathrm{g\cdot mol^{-1}}$
R	universal gas constant (8.31441 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)
T	temperature, K
T_b	boiling point, K
T_c	critical temperature, K
T_r	reduced temperature
P	total pressure of the system, kPa
P_c	critical pressure, kPa
P_i^{S}	vapour pressure of pure component i at the system temperature, kPa
P_r	reduced pressure
$\lvert\Delta P_{aver}\rvert$	absolute average pressure residuals between the measured and calculated pressure, point test criterion
V_i^{L}	molar volume of pure component i in liquid phase at the system temperature, $\mathrm{cm^3\cdot mol^{-1}}$
x_i	mol fraction of component i in the liquid phase
y_i	mol fraction of component i in the vapour phase
$\lvert\Delta y_{aver}\rvert$	absolute average deviations between the measured and calculated mole fractions of the vapour phase, point test criterion
Z_i	composition of component i charged into ebulliometer, g

Greek letters

α	parameter of SRK EOS
γ_i	activity coefficient of component i in the liquid phase
γ_i^{∞}	infinite dilution activity coefficient of component i in the liquid phase

ϕ_i	$= f_i / P$, fugacity coefficient of component *i* in the vapour phase
$\hat{\phi}_i$	$= f_i / y_i P$, partial fugacity coefficient of species *i* in a mixture
ϕ_i^S	pure component saturated liquid fugacity coefficient at the system temperature
$\Lambda_{ij}, \Lambda_{ji}$	Wilson parameters
$\lambda_{ij}, \lambda_{ji}$	exponential parameters in Wilson equation, J/mol
ω	acentric factor

Superscripts

E	excess property
S	saturated
L	liquid
V	vapour

Subscripts

aver	average
c	critical property
calc	calculated
exp	experimental
i,j	components of a mixture
r	reduced property

1 INTRODUCTION

1.1 Sulphur Compounds in Fuels

Crude oil is the main source of liquid fuels. Crude oil is a complex mixture of hydrocarbons, mainly paraffinic, naphthenic, and aromatic compounds, the proportions of which vary according to their origin. Crude oil also contains smaller amounts of sulphur, nitrogen and oxygen compounds, and traces of heavy metals such as vanadium and nickel. The sulphur content of crude oil depends on the crude oil's origin: North African (0.2 wt %); mid-continental US (0.2-2.5 wt %); Venezuelan (2-4 wt %) [1]; North Sea (0.4 wt %), and Russian (1.2 wt %) [2]. Sulphur in crude oil is present as organic sulphur compounds, H_2S, and small amounts of elemental sulphur.

Oil refineries apply physical and chemical processes to treat and refine crude oil into petroleum products, such as liquefied petroleum gas, gasoline, diesel fuel, kerosene, and gas oil. After the salts and other impurities have been removed from the crude oil, the first refinery process is the separation of crude oil into fractions by distillation. These fractions contain sulphur compounds that are later removed in desulphurisation processes in order to meet the product specifications.

The petroleum fractions are defined by either their boiling point range or carbon chain length, as appropriate. The petroleum fractions from distillation, the type and amount of sulphur compounds found in each fraction, and their typical uses are presented in Table 1. The sulphur content increases with an increase in the molecular weight of the fraction. The main sulphur compounds are organic sulphides or disulphides, mercaptans, and thiophenes in the low-boiling fractions. Sulphur is found mainly as thiophene derivatives such as benzo- and dibenzothiophenes in the higher-boiling fractions. The middle fractions may actually contain more sulphur than the higher-boiling fractions as a result of the decomposition of the compounds with a higher molecular weight during distillation.

The thermodynamic properties of the sulphur compounds and the appropriate determination of the vapour liquid equilibrium (VLE) of sulphur compounds are very important in determining the feasibility of the separation of the sulphur compounds from hydrocarbons and the design of separation processes. VLE information on sulphur compounds with hydrocarbons is very limited in the literature. As a consequence, the currently available thermodynamic models are inadequate for predicting both the phase equilibrium and physical properties of mixtures containing the sulphur compounds in the dilute range.

In this work, VLE measurements of several sulphur compounds in selected hydrocarbons were performed to get more information about the VLE of sulphur compounds, which is needed for the calculation and prediction of the phase behaviour and other thermodynamic properties of such systems. The new information is very important for thermodynamic model development and the calculation of the interaction parameters needed to predict the quantities and species present in each product stream.

Table 1. Sulphur compounds in fractional petroleum products [1]

fraction	hydrocarbon and boiling point range (ºC)	typical use	typical sulphur compound in fraction	amount of sulphur compounds as elemental sulphur
gas	up to C_4 ~40	burned as fuel, LPG	H_2S, COS	> 1% weight
straight-run gasoline	C_4-C_5 ~100	blended into gasoline, isomerised, or used as chemical feedstock	low molecular weight thiols, simple sulphides	a few ppm
virgin naphtha (light distillate)	C_5 ~150	used as a feed to catalytic reformer or blended into gasoline	heavy molecular weight thiols, cyclic sulphides, thiophene	a few to hundreds of ppm
heavy naphtha (kerosene)	up to ~C_{15} 120-200	jet fuel, kerosene	sulphides, in acyclic as well as cyclic alkanes, disulphides, alkylthiophenes, benzothiophenes, dibenzothiophenes	hundreds to 2% weight
light gas oil	up to ~C_{20} 200-310	fuel oil or blending stock for jet fuel and/or diesel fuel		0.05-3% weight
gas oil (heavy distillate)	up to ~ C_{25} up to ~350	used as a feed for a catalytic cracker or sold as heavy fuel oil		3-5% weight

1.2 Environmental Issues

The sulphur compounds in petroleum products often produce harmful effects. Their presence creates processing challenges and affects product quality. Many sulphur compounds are toxic, reactive, and corrosive to processing equipment and they damage the catalysts used in further processing. Sulphur compounds impart undesirable odours to gasoline and contribute to gum formation and the deposition of solids in diesel fuel. From the environmental point of view, all sulphur compounds in fuel contribute to acid rain. It is also known that sulphur compounds poison the catalytic converters of modern automobiles.

In order to minimise the health and environmental effects of automotive exhaust emissions and improve vehicles' fuel efficiency, stricter regulations on sulphur levels in liquid fuels have been applied in most countries. The sulphur levels in the gasoline, diesel and jet fuels are being lowered. The new allowable levels for gasoline vary: 30 ppm in Canada since 2004; 50

ppm in Europe since 2005, and 30 ppm in United States since 2006 [3]. Ultra low-sulphur gasoline (< 5 ppm) will be required in the coming 5-10 years. For diesel, EU has set a sulphur content limit of 50 ppm since 2005 [4], and the United States has determined a limit of 15 ppm by 2007 [5]. The US sulphur regulation for jet fuel is a maximum of 3000 ppm in 2006 and less than 3000 ppm by 2010 [5]. Such ultra-low-sulphur fuel requirements force refineries to increase the efficiency of their desulphurisation processes and to improve their sulphur removal technologies.

1.3 Removal of Sulphur Compounds

Hydrodesulphurisation (HDS) is the conventional hydrotreating method for the removal of sulphur compounds from hydrocarbon streams [6]. Additional pre- or post-treatment of the feed to compensate for octane loss can be coupled with the HDS process. In typical hydrodesulphurisation processes, a portion of the sulphur components is converted by reaction with hydrogen gas in the presence of a suitable catalyst to form hydrogen sulphide.

The design of the separation process to accomplish the removal of sulphur compounds in dilute systems requires knowledge of the vapour-liquid equilibrium (VLE) of sulphur compounds with hydrocarbons and, particularly, the activity coefficient at infinite dilution (γ^{∞}); hence knowledge of the VLE of sulphur compounds in various hydrocarbons is essential for the design and operation of sulphur compound distribution in a distillation column.

Many of the organosulphur compounds contained in low-boiling crude oil fractions have lower thermal stability than hydrocarbons; in particular, mercaptans, sulphides, and disulphides are very reactive, and thus they can easily be removed effectively from the streams after being converted into hydrogen sulphide. The off-gas containing hydrogen sulphide can be removed from the product gas stream by the use of a wash solvent (such as amine), followed by conversion of the hydrogen sulphide to elemental sulphur in a Claus plant.

In higher-boiling oil fractions such as naptha and diesel, organosulphur compounds contain predominantly thiophenic rings. These compounds include thiophenes and benzothiophenes and their alkylated derivatives. These thiophene-containing compounds are very difficult to convert via a hydrodesulphurisation process. The remaining sulphur compounds left in the hydrocarbon stream and higher-boiling sulphur compounds are removed from the hydrocarbons by distillation.

1.4 Systems of Interest

The VLE of sulphur compounds and hydrocarbons published in the open literature have been extensively reviewed and collected in a matrix format as presented in Appendix 1. The information gathered includes: vapour-liquid equilibrium (VLE) from DECHEMA data series [7-10], the Gas Processor Association [11, 12], and Giles *et al.* [13, 14]; infinite dilution activity coefficients [15], excess molar enthalpies [16-20], and azeotropic data on organic sulphur compounds and hydrocarbons measured [21-24]. In addition, the vapour pressures and physical properties of sulphur compounds were also collected.

The available VLE measurements for hydrogen sulphide, carbon disulphide, and light mercaptans (methanethiol, ethanehiol, and propanethiol) with hydrocarbons (C_1-C_6, C_{10}, and C_{20}) are quite numerous, whereas very few are available for dimethyl sulphide, for which only measurements with light hydrocarbons (C_1-C_5) are available, and for thiophene, for which only measurements with certain hydrocarbons (C_6-C_7) are available.

The available infinite dilution activity coefficients are very scarce, existing only for carbon disulphide with benzene, toluene, *n*-heptane, *n*-octane, 2,2,4-trimethylpentane, *n*-octadecane, and benzyl biphenyl; for thiophene with diphenyl methane, *n*-hexadecane, *n*-octadecane and octacosane, and for ethanethiol, 1-propanethiol, 1-butanethiol, 2-butanethiol, dimethyl sulphide, diethyl sulphide, methyl ethyl sulphide, and diethyl disulphide with *n*-hexadecane.

The available excess enthalphies are mostly found for several sulphides and disulphides with *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-docecane, and *n*-hexadecane.

Because of the lack of experimental data, the process simulation programs failed to adequately predict the measured distribution of the volatile organic sulphur compounds typically found in natural gas liquid fractionators [25], causing large errors compared to the data compiled at the pilot plant [26]. Several models in the simulator program gave different results for one system, indicating that more evaluation and experimental data are needed to revise those parameters for which poor results are obtained.

The original UNIFAC model developed by Fredenslund *et al.* [27], modified by Gmehling *et al.* [28], and revised and extended by Wittig *et al.* [29, 30] have been widely applied in the estimation of the VLE properties of organic mixtures, as it includes almost all of the functional groups involved in the organic substances. However, the applications of the predictive models are limited since some important interaction parameters for the sulphur and hydrocarbon functional group are unavailable. The important UNIFAC sulphur and hydrocarbon group interactions are shown in Table 2. The missing interaction parameters of the functional group are CH_3SH with C=C, CH_2S with C=C, ACH, $ACCH_2$, CH_2O, and C_4H_4S with C=C, CH_2O. The missing important parameters in the UNIFAC model can be determined from experiments, and thus the VLE of the systems containing these missing groups should be measured.

Table 2. Important UNIFAC sulphur and hydrocarbon group interactions

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

(√) available
(–) not available

Many important VLE sets of various sulphur compounds and hydrocarbons (C_4-C_{10}, cycloalkanes, alkenes, aromatics) should be measured, especially light and heavy mercaptans (C_3-C_{10}-thiol), sulphides (dimethyl sulphide, diethyl sulphide, C_2-C_{10}-S), disulphides (C_2-C_{10}-S_2), and thiophenes (alkyl thiophenes). The behaviour of sulphur compounds with alkanes, alkenes, and ether should also be studied in order to perform accurate phase equilibria modelling.

As part of our sulphur project measurements, the work in this thesis consists of 2 parts. The first part is VLE measurements of 1-propanethiol, diethyl sulphide, and thiophene with hydrocarbons (C_6 to C_8) and 2-ethoxy-methylpropane carried out under isobaric and isothermal conditions with a circulation still of the Yerazunis type [31]. The behaviour of sulphur compounds with alkanes and alkenes was also studied. The VLE systems measured with a recirculation still are shown in Table 3.

Table 3. VLE measurements with recirculation still

component 1 / component 2	1-propanethiol	thiophene	diethyl sulphide
n-hexane	–	isothermal 323.15 K, 333.15 K	isothermal 323.15 K, 333.15 K
1-hexene	isobaric, 101.3 kPa isothermal, 328.15 K	isothermal 323.15 K, 333.15 K	isothermal 323.15 K, 333.15 K
cyclohexane	–	–	isothermal 343.15, 353.15 K
***n*-heptane**	–	–	isothermal 353.15 K, 363.15 K
toluene	isobaric 90.03 kPa	isobaric 90.03 kPa	isobaric 90.03 kPa
2,2,4-trimethylpentane	–	isothermal 343.15 K, 353.15 K	isothermal 353.15 K, 363.15 K
2-ethoxy-methylpropane	–	isothermal 333.15 K, 343.15 K	isothermal 333.15 K, 343.15 K

(–) no measurements

The VLEFIT program [32] was used for calculating the activity coefficients and infinite dilution activity coefficients. The gamma-phi approach was used in the calculation of vapour-liquid equilibria. The activity coefficients of the liquid phase (gamma) were correlated with the Wilson model. The fugacity of the vapour phase (phi) was calculated with the Soave-Redlich-Kwong (SRK) model [33]. The measured VLE was also compared with the predicted VLE from the original UNIFAC, UNIFAC-Dortmund, and COSMO-RS [34] predictive models. All the data found in the literature were used together with the new consistent measurements to improve and develop the thermodynamic models in dilute systems.

The second part is γ^{∞} measurements of several organic sulphur compounds in selected hydrocarbons with comparative Swietoslawsky-type ebulliometry [35] under various isobaric conditions. This technique is a simple, fast, and accurate method for measuring activity coefficients at infinite dilution for systems with a relative volatility not too far from unity [36]. Dilute binary system of 1-propanethiol, ethyl methyl sulphide, and thiophene in toluene, *n*-heptane, and 2,2,4-trimethylpentane were measured at 90 kPa. The infinite dilution activity coefficients determined were compared with the data from the literature, the predictive original UNIFAC group contribution model, and also with infinite dilution activity coefficients obtained from VLE measurements using the recirculation still apparatus.

2 THERMODYNAMIC PRINCIPLES

The theory of vapour-liquid equilibrium can be found in depth in the thermodynamic textbooks [37-39]. A brief summary of the fundamental equations needed in this study is given.

2.1 Vapour-Liquid Equilibrium Concept

The condition of thermodynamic equilibrium in a two-phase (vapour and liquid) multicomponent system is

$$f_i^{\mathrm{V}} = f_i^{\mathrm{L}} \tag{1}$$

where f_i^{V} and f_i^{L} are the fugacities of component *i* in the vapour or liquid phase, respectively. The gamma-phi approach was used in the calculation of vapour-liquid equilibria. The gas phase behaviour of the mixture can be described by several of the equations of state, whereas the liquid phase nonideality can be described by any of the activity coefficient models (also called excess Gibbs free energy models).

2.1.1 Vapour fugacity

The concentration dependence of the vapour phase fugacity f_i^{V} is given by

$$f_i^{\mathrm{V}} = y_i \phi_i P \tag{2}$$

where y_i is the mole fraction and ϕ_i is the fugacity coefficient of component *i* in the vapour phase.

The fugacity coefficient for pure component *i* is calculated by the equation:

$$\phi_i = \frac{f_i}{P} \tag{3}$$

For the calculation of the fugacity coefficient of component *i* in mixtures, an equation of state (EOS) such as those of van der Waals, Soave-Redlich-Kwong [33], or Peng Robinson [40] can be used. In this thesis, the SRK EOS was used in the calculation of the vapour phase fugacity coefficient. The Soave-Redlich-Kwong EOS was the first modification of the simple Redlich-Kwong EOS where the parameter *a* was made temperature-dependent. The parameters of pure compound: T_c, P_c and ω needed in the SRK-EOS were taken from the literature [41]. The SRK formula for calculating the fugacity coefficient of species *i* in the mixture:

$$\ln \hat{\phi}_i = \frac{B_i}{B}(z-1) - \ln(z-B) + \frac{A}{B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j (a\alpha)_{ij}\right] \ln\left(1+\frac{B}{z}\right) \tag{4}$$

The SRK EOS standard form is given by:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \tag{5}$$

Pure-component parameters:

$$a = 0.42747\frac{R^2 T_c^2}{P_c} \qquad b = 0.08664\frac{RT_c}{P_c} \tag{6 a\&b}$$

$$\alpha = \left[1 + \left(0.48508 + 1.55171\omega - 0.15613\omega^2\right)\left(1-\sqrt{T_r}\right)\right]^2 \tag{7}$$

$$A = \frac{a\alpha P}{R^2 T^2} = \frac{0.42747\alpha P_r}{T_r^2} \qquad B = \frac{bP}{RT} = \frac{0.08664 P_r}{T_r} \tag{8 a\&b}$$

In its polynomial form Equation (5) becomes:

$$z^3 - z^2 + \left(A - B - B^2\right)z - AB = 0 \tag{9}$$

The mixing rules were applied to calculate the mixture parameters A and B.

$$a\alpha = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j \left(a\alpha\right)_{ij} \qquad b = \sum_{i=1}^{N} y_i b_i \tag{10 a\&b}$$

$$A = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j A_{ij} \qquad B = \sum_{i=1}^{N} y_i B_i \tag{11 a\&b}$$

where

$$\left(a\alpha\right)_{ij} = \left(1 - k_{ij}\right)\sqrt{\left(a\alpha\right)_i \left(a\alpha\right)_j} \tag{12}$$

The binary interaction parameters, k_{ij}, in the quadratic mixing rules were set to zero, because at low pressure the systems are almost ideal. In those cases the effect of binary interaction is also very small.

2.1.2 Liquid fugacity

The liquid phase fugacity f_i^{L} of component i is given by

$$f_i^{\mathrm{L}} = x_i \gamma_i f_i^{\mathrm{S}} \tag{13}$$

where f_i^{S} is the standard state fugacity, x_i is the mole fraction, and γ_i the activity coefficient of component i in the liquid phase. γ_i is calculated using G^{E} models.

The fugacity f_i^{S} of the pure liquid is related to its vapour pressure, P_i^{S}:

$$f_i^{\mathrm{L}} = P_i^{\mathrm{S}} \phi_i^{\mathrm{S}} \exp\left(\frac{1}{RT}\int_{P_i^{\mathrm{S}}}^{P} V_i^{\mathrm{L}} dP\right) \tag{14}$$

The expression $\exp\left(\frac{1}{RT}\int_{P_i^{\mathrm{S}}}^{P} V_i^{\mathrm{L}} dP\right)$ is called Poynting correction (POY), which allows for the influence of the change of the pressure on fugacity from P to P_i^{S}.

By combining Equations (1), (3), (13), and (14), we obtain the general equations for equilibrium of component i between the vapour and liquid phases:

$$y_i \phi_i P = x_i \gamma_i P_i^{\mathrm{S}} \phi_i^{\mathrm{S}} \exp\left(\int_{P_i^{\mathrm{S}}}^{P} \frac{V_i^{\mathrm{L}}}{RT} dP\right) \tag{15}$$

where y_i is the mole fraction of component i in the vapour phase, P is the total pressure of the system, ϕ_i is the fugacity coefficient of component i in the vapour phase, x_i is the mole fraction of component i in the liquid phase, P_i^S is the vapour 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 the liquid phase at the system temperature, T is the temperature in Kelvin, and R is the universal gas constant.

The VLEFIT program was used for processing all measurements. The Soave-Redlich-Kwong equation of state with quadratic mixing rules in the attractive parameter and linear in co-volume was used for vapour-phase fugacity coefficient calculation. The binary interaction parameter in the quadratic mixing rules was set to zero. The Rackett equation [42] was used to calculate the liquid molar volume in the Poynting factor. The Antoine parameters for all compounds were regressed from the vapour pressure measured in this work. The critical temperature, critical pressure, acentric factor, and the liquid molar volume for each component used in the calculations are taken from the literature [41].

2.2 Correlation of Liquid Phase Activity Coefficient

Liquid activity models are used to model liquid phase activity coefficients and their parameters are fitted against VLE experiments. Among many existing models, Wilson [43], NRTL (Non-Random Two-Liquid) [44], and UNIQUAC (Universal Quasi-Chemical) [45] are widely used. Each model has its specific interaction parameters for each component pair. In this thesis the Wilson equation is used for calculating the activity coefficient because it represented the systems being studied very well.

The Wilson model is applicable to multi-component mixtures. The Wilson model expression for the excess Gibbs energy of binary systems is defined as

$$\frac{g^E}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12}x_2\right) - x_2 \ln\left(x_2 + \Lambda_{21}x_1\right) \tag{16}$$

The activity coefficient equations calculated by Wilson models are given in equation:

$$\ln\gamma_1 = -\ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \tag{17}$$

and

$$\ln\gamma_2 = -\ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \tag{18}$$

The interaction parameters Λ_{12} and Λ_{21} are expressed as

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \qquad \Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left(-\frac{\Delta\lambda_{21}}{RT}\right) \tag{19 a\&b}$$

where $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are binary parameters.

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

$$\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}\left(\frac{T}{K}\right) + a_{2,ij}\left(\frac{T}{K}\right)^2 \tag{20}$$

where

$$\Delta\lambda_{12} = \lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}\left(\frac{T}{K}\right) + a_{2,12}\left(\frac{T}{K}\right)^2 \tag{21}$$

$$\Delta\lambda_{21} = \lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}\left(\frac{T}{K}\right) + a_{2,21}\left(\frac{T}{K}\right)^2 \tag{22}$$

g^E is the molar excess Gibbs energy, R is the gas constant, T is the temperature, γ_i is the activity coefficient of component i, x_i is the liquid phase mole fraction of component i, Λ_{ij} and λ_{ij} are the binary parameters of components i and j , V_i^{L} is the molar volume of pure liquid component i.

The use of temperature-dependent Wilson parameters allows a good simultaneous description of vapour-liquid equilibrium and excess enthalpy data [IV], [V], [VI].

2.3 Excess Enthalpy

The molar excess enthalpy, H^{E}, is defined as the heat absorbed when one mole of the mixture is made up from the pure compounds at the specified temperature and pressure. The H^{E} describes the temperature dependence of the activity coefficients following the Gibbs-Helmholtz equation:

$$H^{\mathrm{E}}_{\mathrm{calc}} = -RT^2\left(\sum_{i=1}^{NC} x_i \frac{\partial\left(\ln\gamma_{i,\mathrm{calc}}\right)}{\partial T}\right)_{P,x} \tag{23}$$

The temperature-dependent parameters of the Wilson model (Eqs 21 & 22) can be obtained by simultaneously using VLE and excess enthalpy (H^{E}) measurements. This procedure normally leads to models that are applicable across a wide temperature range [IV], [V], and [VI].

The measurements of vapour-liquid equilibria and excess enthalphy from the literature of binary system diethyl sulphide + *n*-heptane [IV], diethyl sulphide + *n*-hexane [V], and diethyl sulphide + cyclohexane [VI] were represented simultaneously by the Wilson equations with quadratic temperature dependent parameters.

The comparison between the measured excess molar enthalpy [18] and that calculated by the extended Wilson model (obtained from VLE measurements and H^{E} data [18]) for the diethyl sulphide + *n*-heptane system at 303.15 K is shown in Figure 1. Good agreement is obtained between the experimental and calculated results. The calculated excess enthalpy using the Wilson model obtained from the VLE measurements is included in Figure 1. The agreement between experimental and calculated excess molar enthalpy can be considered typical for the VLE measured with this apparatus [46].

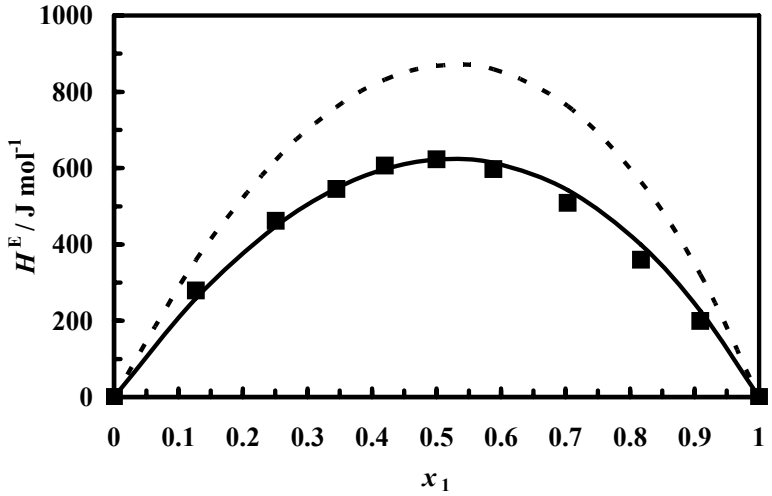

Figure 1 Excess molar enthalpy for the diethyl sulphide (1) + *n*-heptane (2) system at 303.15 K: ■, measured [18]; –, from the Wilson model (VLE this work + H^E literature [18]); - - -, from the Wilson model (VLE this work).

The comparison between the measured excess molar enthalpy [19] and that calculated using the parameters from the extended Wilson model (VLE this work + H^E literature [19]) for diethyl sulphide + *n*-hexane system at 318.5 K is shown in Figure 2. Good agreement is obtained between the experimental and calculated results.

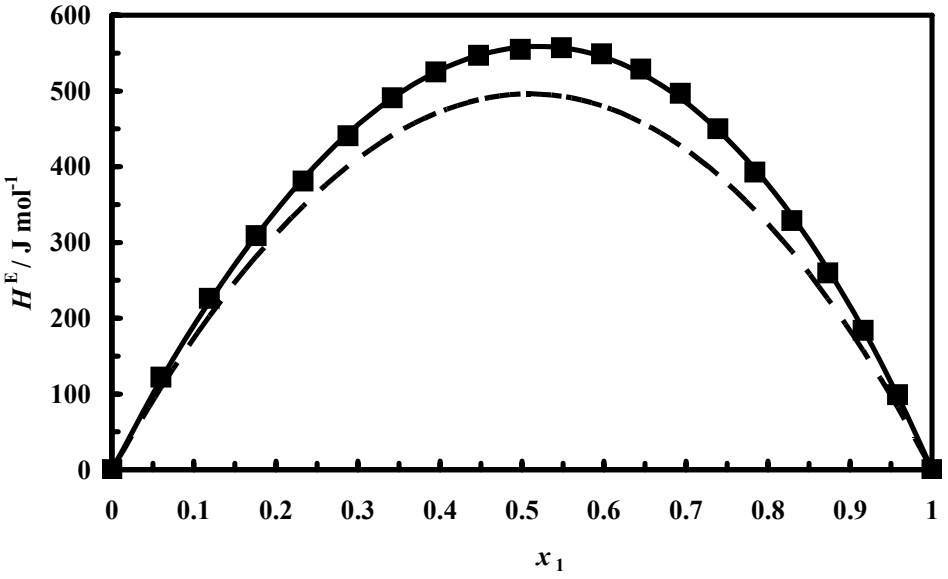

Figure 2 Excess molar enthalpy at 318.15 K for the diethyl sulphide (1) + *n*-hexane (2) system: ■, measured [19]; –, from the Wilson model-extended data (VLE this work + H^E literature [19]). Excess molar enthalpy at 318.15 K for the diethyl sulphide (1) + 1-hexene (2) system: – –, calculated from the Wilson model (VLE this work).

The temperature-dependent parameters of the Wilson model for diethyl sulphide + cyclohexane system were fitted by simultaneously using the measured VLE data at (353.15 K and 343.15 K and excess enthalpy (H^E) measurements [20] at 298.15 K. The comparison between the measured excess molar enthalpy [20] and that calculated using the parameters from the extended Wilson model for diethyl sulphide + cyclohexane system is shown in Figure 3. Good agreement is obtained between the experimental and calculated results.

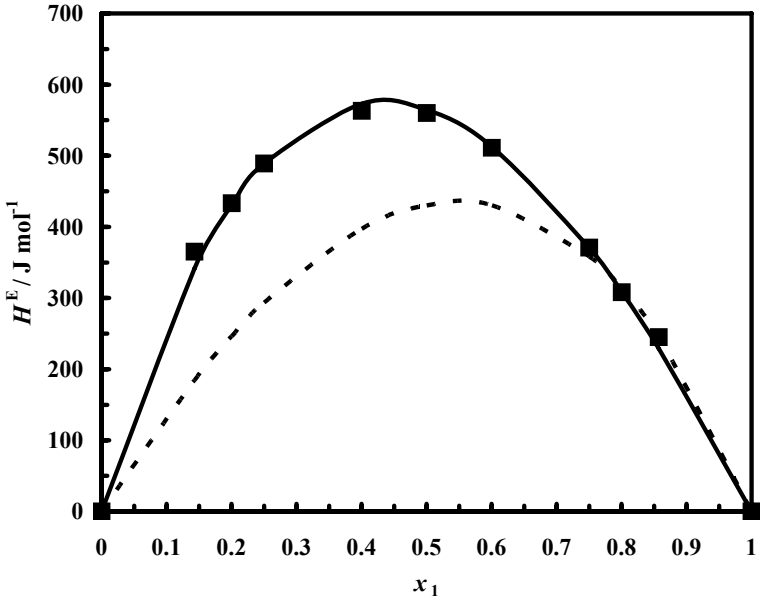

Figure 3 Excess molar enthalpy at 298.15 K for the diethyl sulphide (1) + cyclohexane (2) system: ■, measured [20]; –, from the Wilson model-extended data (VLE this work + H^E literature [20]). Excess molar enthalpy at 298.15 K for the diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) system: - - -, calculated from the Wilson model (VLE this work).

The excess molar enthalpies can be obtained from the vapour-liquid equilibrium measurements. Excess molar enthalpies for the diethyl sulphide + 1-hexene and diethyl sulphide + 2-ethoxy-2-methylpropane systems were calculated from the VLE measurements. The excess enthalpies at 318.15 K for the diethyl sulphide + 1-hexene system were calculated from the Wilson model obtained from VLE measurements. The results are shown in Figure 2. The excess enthalpies at 298.15 K for the diethyl sulphide + 2-ethoxy-2-methylpropane system were calculated from the VLE measurements. The results are shown in Figure 3.

2.4 Parameter Fitting and Objective Function

The VLEFIT program was used for processing the measurements and H^E. After the parameters of VLE models have been optimised by minimising the selected objective function (OF), the activity coefficient models are calculated by optimised model parameters and then compared with the measurements.

The objective function (OF) is the deviation between the measurements and the VLE model prediction. The selection of the objective function used depends on the VLE measurements

(isothermal or isobaric and availability data sets). The following objective functions were used:

$$\mathrm{OF} = \frac{1}{N_{VLE}} \sum_{i=1}^{N_{VLE}} \left(\frac{P_{\mathrm{i,calc}} - P_{\mathrm{i,exp}}}{P_{\mathrm{i,exp}}} \right)^2 \qquad \text{[I]} \qquad (24)$$

$$\mathrm{OF} = \frac{1}{N_{VLE}} \sum_{i=1}^{N_{VLE}} \left(\frac{\left| \gamma_{\mathrm{i,calc}} - \gamma_{\mathrm{i,exp}} \right|}{\gamma_{\mathrm{i,exp}}} \right) \qquad \text{[III], [IV], [V], [VI], [VII]} \qquad (25)$$

$$\mathrm{OF} = \frac{1}{N_{\mathrm{VLE}}} \sum_{i=1}^{N_{\mathrm{VLE}}} \left(\frac{\left| \gamma_{\mathrm{i,calc}} - \gamma_{\mathrm{i,exp}} \right|}{\gamma_{\mathrm{i,exp}}} \right) + \frac{1}{N_{\mathrm{HE}}} \sum_{i=1}^{N_{\mathrm{HE}}} \frac{\left| H^{\mathrm{E}}_{\mathrm{i,calc}} - H^{\mathrm{E}}_{\mathrm{i,exp}} \right|}{\mathrm{kJ \cdot mol^{-1}}} \qquad \text{[IV], [V], [VI]} \qquad (26)$$

2.5 Differential Ebulliometry

Gautreaux and Coates [47] developed thermodynamic equations for the direct experimental measurement of the activity coefficient at infinite dilution (γ_i^{∞}) for the ratio of activity coefficient $\left(\gamma_i^{\mathrm{L}} / \gamma_i^{\mathrm{V}}\right)^{\infty}$. However, the equations are complex and difficult to use. The simplifications were made with the assumption of an ideal gas vapour phase and neglect the Poynting correction.

For isobaric measurement, the equation for the γ_i^{∞} included the correction for vapour-phase nonideality based on the truncated virial equation given by [48]:

$$\gamma_i^{\infty} = \frac{\varepsilon_i^{\infty} P_j^{\mathrm{S}}}{P_i^{\mathrm{S}}} \left[1 - \beta \frac{d \ln P_j^{\mathrm{S}}}{dT} \left(\frac{\partial T}{\partial x_1} \right)_P^{\infty} \right] \qquad (27)$$

where

$$\varepsilon_i^{\infty} = \exp\left[\frac{\left(B_{ii} - V_i^{\mathrm{L}}\right)\left(P_j^{\mathrm{S}} - P_i^{\mathrm{S}}\right) + \delta_{ij} P_j^{\mathrm{S}}}{RT} \right] \qquad (28)$$

$$\beta = 1 + P_j^{\mathrm{S}} \left(\frac{B_{22} - V_j^{\mathrm{L}}}{RT} \right) \qquad (29)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (30)$$

where B_{ij}, B_{ii}, and B_{jj} are the second virial coefficient [49], P_i^{S} is the vapour pressure of pure component *i* at the system temperature, and V_i^{L} is the liquid molar volume of pure component *i*, *T* is the temperature in Kelvin, and *R* is the universal gas constant.

These equations indicate that for isobaric measurements γ_i^{∞} can be obtained directly from the limiting slopes of temperature vs. composition plots. The experimental data are used to determine the limiting slope at infinite dilution $(\partial T/\partial x_1)_P^{\infty}$, which was fitted to the second degree polynomial:

$$\Delta T = a x_i + b x_i^2 \qquad (31)$$

The limiting slope $(\partial T/\partial x_1)_P^{\infty}$ was determined from the value of *a*. As a result of phase splitting into vapour and liquid phases, the liquid composition in the equilibrium (x_i) is not the same as the gravimetrically prepared solution charged into the ebulliometer (Z_i). Consequently, the evaporation factor (*f*) is required to obtain liquid concentration at the equilibrium. Once *f* has been determined, the concentration in the equilibrium is calculated by:

$$x_i = Z_i\left(\frac{1+f}{1+K_i f}\right) \tag{32}$$

The evaporation factor was determined from *n*-hexane (1) and ethyl acetate (2) experiments at 74.0 kPa, 340 K at different compositions. The average *f* value is 0.055, which agreed well with Raal's analysis [50].

3 PREDICTION OF LOW PRESSURE VAPOUR-LIQUID EQUILIBRIUM

3.1 UNIFAC (UNIQUAC Functional Group Activity Coefficient)

Group contribution methods can be applied to predict the phase equilibrium behaviour. The original UNIFAC and modified UNIFAC-Dortmund are predictive methods which treat the liquid mixture as a mixture of structural groups. Fredenslund *et al.* [27] described the theory of the original UNIFAC and its applications in detail. The liquid activity coefficient is assumed to be the sum of the contributions of the individual structural groups, where the activity coefficients in the mixture are related to interactions between structural groups.

The method combines the solution of functional groups concept with a model for activity coefficients based on an extension of UNIQUAC. The sizes and areas of individual functional groups were evaluated from pure component and molecular structure data. The interaction parameters representing the energetic interactions between groups (a_{ij}) were fitted from VLE databases. Wittig *et al.* [29, 30] have published the most recent parameter tables for the original UNIFAC and UNIFAC-Dortmund, respectively. Compared to the original UNIFAC, UNIFAC-Dortmund has a better description of the temperature dependency, which was parameterised separately for each pair of groups.

The experimental results obtained in this work were correlated with the Wilson model and also compared with the original UNIFAC and UNIFAC-Dortmund predictive models. However, as a result of the unavailability of the interaction functional group parameters presented in Table 2, the original UNIFAC and UNIFAC-Dortmund are unable to describe the behaviour of some of the systems measured, as shown in Table 4.

Table 4. Original UNIFAC and UNIFAC-Dortmund prediction for system measured

component 1 / component 2	1-propanethiol	thiophene	diethyl sulphide
***n*-hexane**	–	available	available
1-hexene	not available (CH_2-SH-CH_2=CH)	not available (C_4H_4S - CH_2=CH)	not available (CH_2S- CH_2=CH)
cyclohexane	–	–	available
***n*-heptane**	–	–	available
toluene	available	available	not available (CH_2S-ACH)
2,2,4-trimethylpentane	–	available	available
2-ethoxy-methylpropane	–	not available (C_4H_4S- CH_2O)	not available (CH_2S- CH_2O)

(–) no measurements

3.2 COSMO-RS (Conductor-like Screening Model for Real Solvents)

When the UNIFAC and UNIFAC-Dortmund group contribution methods are not applicable, COSMO-RS can be used as an alternative method for the prediction of vapour-liquid equilibrium. The name COSMO-RS is derived from "conductor-like screening model" (COSMO) [51], which is an efficient variant of dielectric continuum solvation methods in quantum chemical programs, and its extension to "real solvents" (RS) [52]. COSMO-RS is a statistical thermodynamics approach based on the results of quantum chemical COSMO calculations. Klamt has described COSMO-RS theory in detail [53]. A brief introduction to COSMO-RS is provided.

COSMO-RS calculation is a two-step procedure. In the first step, quantum chemical calculations have to be performed for all compounds of interest. In these calculations, the continuum solvation model COSMO is applied in order to simulate a virtual conductor environment for the molecule. In this environment, the solute molecule induces a polarisation charge density σ on the interface of the molecule to the conductor, i.e. on the molecular surface, and these charges act back to the solute, generating a more polarised electron density than in a vacuum. During the quantum chemical self-consistency algorithm, the solute molecule is converged to its energetically optimal state in a conductor with respect to electron density and geometry. The standard quantum chemical method for COSMO-RS is density functional theory (DFT) with a triple zeta valence polarised basis set (TZVP). All DFT/COSMO calculations were performed using the quantum chemical program TURBOMOLE version 5.7 [54]. Geometry optimisation for the molecules under investigation was also performed with Turbomole software. Subsequent COSMO-RS calculations were performed with COSMOtherm-C12-0105 [55]. In the second step of COSMO-RS, the statistical thermodynamics of the molecular interactions, the polarisation charge density is used for the quantification of the interaction energy of surface segments interacting pair-wise with regard to the most important molecular interaction modes, i.e. electrostatics and hydrogen bonding. The less specific van der Waals (vdW) interactions or dispersive interactions are taken into account in a more approximate way by element-specific dispersion coefficients.

In the COSMO calculation, the experimentally determined pure component vapour pressures were used because COSMO-RS provided very unsatisfactory prediction of pure component vapour pressures. Pure component vapour pressures predicted with COSMO-RS were higher than the experimental ones. As an example the estimated vapour pressure of 1-propanethiol is presented in Figure 4. The absolute average deviation of the pressure of 1-propanethiol between COSMO-RS prediction and the experimental result was 27 kPa. Similar results were obtained for the other compounds.

As can be seen from Figure 14 to Figure 29, in general, the COSMO-RS predictions for sulphur-containing systems are poorer than the original UNIFAC and UNIFAC-Dortmund methods. The modification of the COSMO-RS model by excluding of the van der Waals interaction from the binary surface interaction energy improves the quality of the prediction. The modified COSMO-RS model was applied to the following systems: 1-propanethiol + toluene, thiophene + toluene, and diethyl sulphide + toluene. The results of the prediction of our VLE systems with the modified COSMO-RS are shown in Figure 5, Figure 6, and Figure 7.

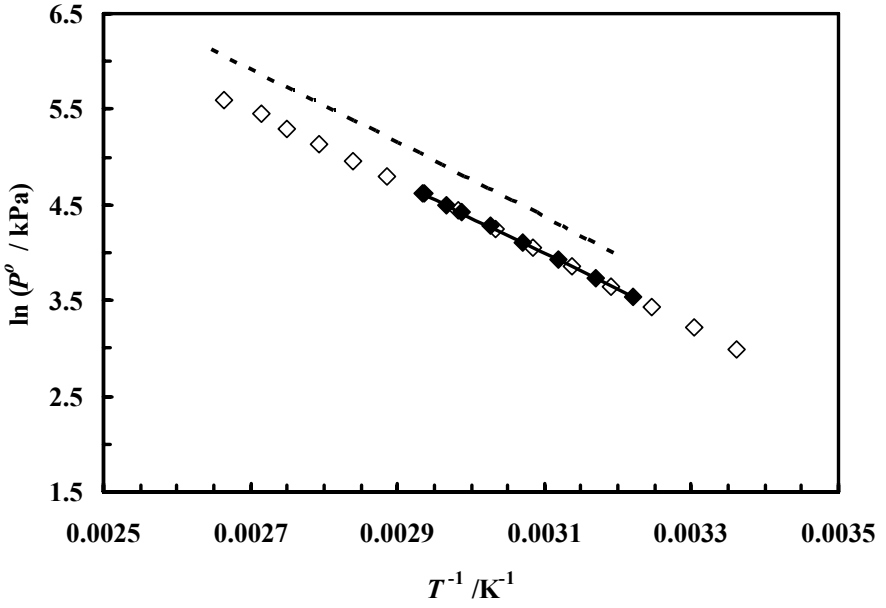

Figure 4 Vapour pressures of 1-propanethiol: ◆, measured; ◇, literature [56]; —, calculated from literature correlation [41]; - - -, COSMO-RS

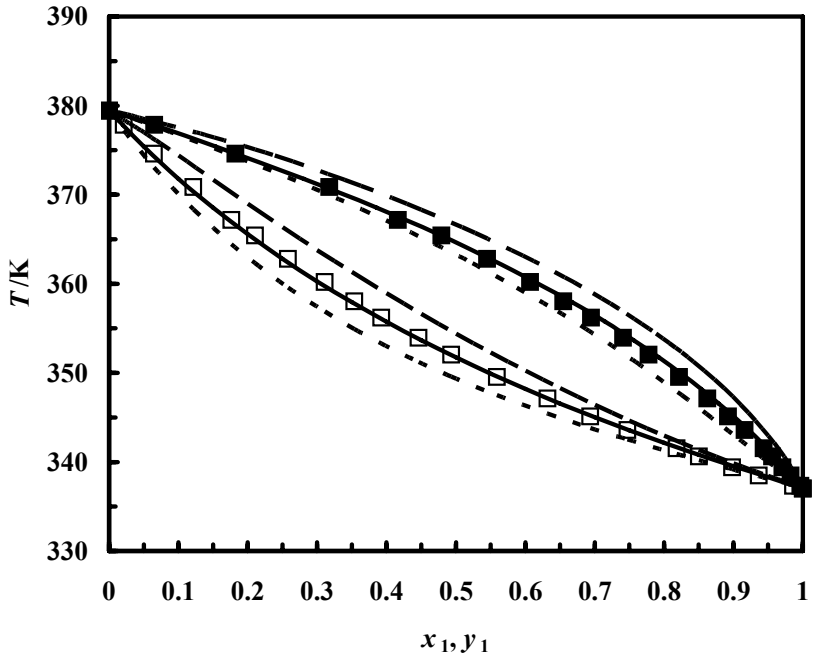

Figure 5 Temperature-composition diagram for the 1-propanethiol (1) + toluene (2) system at 90.03 kPa: □, x_1 measured; ■, y_1 measured; —, COSMO-RS, modified; – –, COSMO-RS; - - -, original UNIFAC.

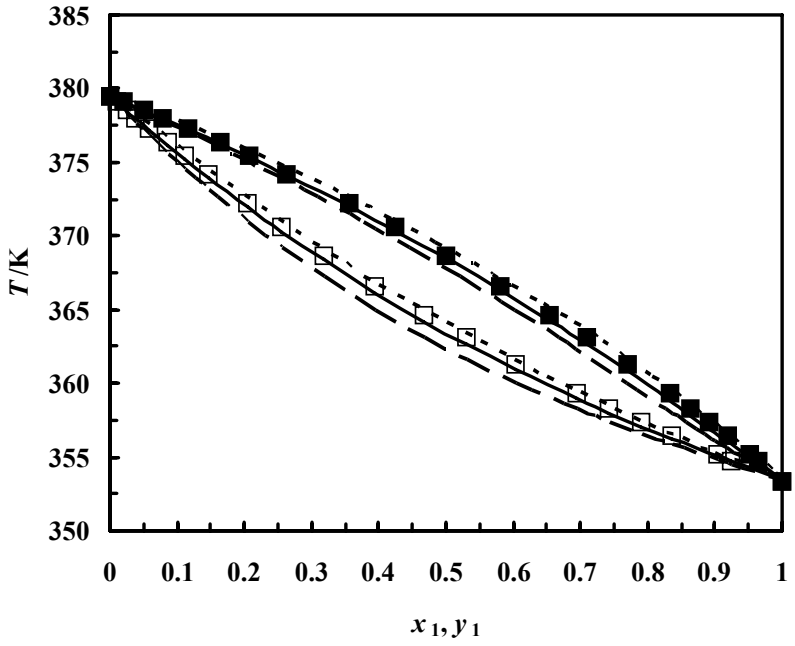

Figure 6 Temperature-composition diagram for the thiophene (1) + toluene (2) system at 90.03 kPa: □, x_1 measured; ■, y_1 measured; —, UNIFAC-Dortmund; – –, original UNIFAC; - - -, COSMO-RS.

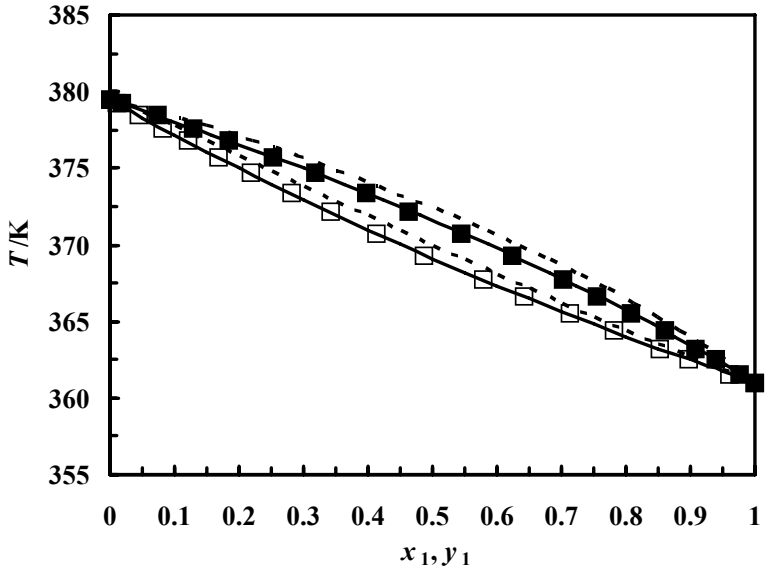

Figure 7 Temperature-composition diagram for the diethyl sulphide (1) + toluene (2) system at 90.03 kPa: □, x_1 measured; ■, y_1 measured; —, COSMO-RS, modified; - - -, COSMO-RS.

4 EXPERIMENTAL SETUP AND PROCEDURES

4.1 Circulation Still VLE Measurements

4.1.1 Experimental setup

The VLE runs were conducted with a Yerazunis-type circulation still [31] built in the glass workshop of Helsinki University of Technology with minor modifications to the original design [57]. The experimental schematic setup is presented in Figure 8. Approximately 80 ml of reagents were needed to run each experiment. The circulation still is placed in a well-ventilated hood to minimise the emission of the sulphur compound to the surroundings.

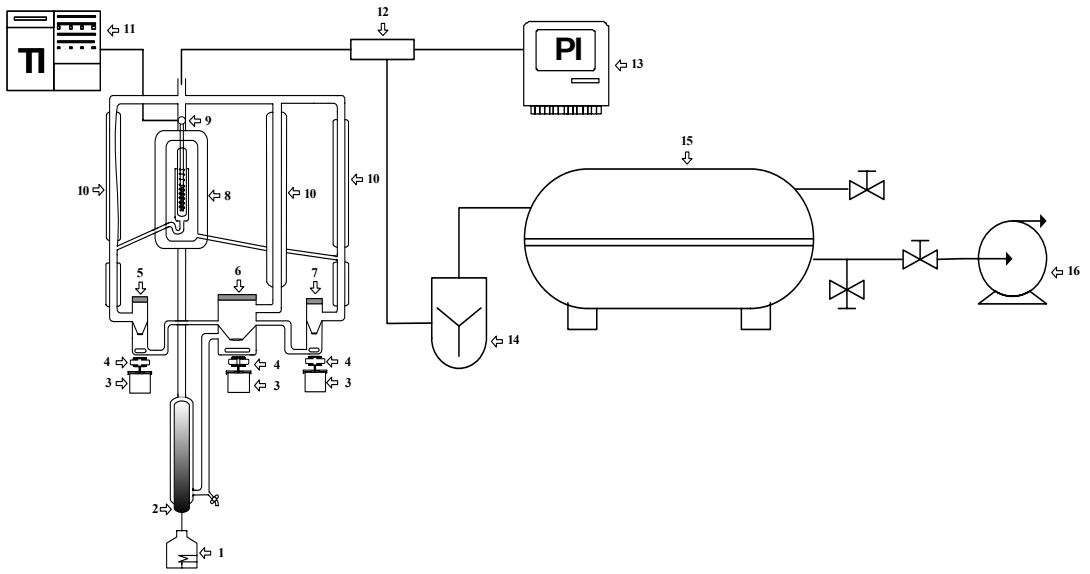

Figure 8 The experimental setup for circulation still apparatus: (1) heating source; (2) immersion heater; (3) DC electric motor; (4) magnetic stirrer bar; (5) liquid phase chamber; (6) mixing chamber; (7) vapour phase chamber; (8) equilibrium cell; (9) thermometer; (10) condenser; (11) temperature indicator; (12) pressure transducer; (13) pressure indicator; (14) N_2 trap; (15) 50 dm^3 ballast; (16) vacuum pump.

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 a thermometer (F200, Tempcontrol), which has a manufacturer's stated 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 instrument 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.

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

4.1.2 Experimental procedures

4.1.2.1 Purity determination

The purity, water content, and refractive indexes of the substances were checked prior to the experiments. The substances were dried over molecular sieves (Merck 3A) for 24 h. The sulphur compounds were used as purchased, without further purification. The purity was checked using gas chromatography (GC) equipped with a flame ionisation 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 an accuracy of ± 0.00002 and the water content was determined with a DL38 KF Titrator (Mettler Toledo).

4.1.2.2 VLE measurements

Pure component 1 was introduced into the circulation still and its vapour pressure was measured at several temperatures. Then component 2 was introduced into the circulation still. It took approximately 15 to 30 minutes to achieve a 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 vapour and liquid samples were withdrawn with a 1-ml Hamilton Sample Lock syringe and after that injected into a cooled 2 ml auto sampler vial containing approximately 1 ml of solvent. The compositions of both samples were immediately measured by gas chromatography (GC) and a refractometer. To prevent the unpleasant odour of the sulphur compounds spreading, the GC and refractometer were placed in a closed and ventilated cupboard.

4.1.2.3 Analysis of VLE

The liquid and vapour phase composition were determined with gas chromatography [I]-[VII]. In addition to the GC analysis, the samples were analysed with refractometry [II] and [III]. 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 maximum error of liquid and vapour composition measurements analysed with GC and refractometry was estimated to be 0.001 mole fraction.

4.1.2.3.1 Gas chromatography

The pure components were used to determine the retention times, after which the GC was calibrated with 15 mixtures of known composition that were prepared gravimetrically. To reduce the volume of the sample, 1 ml of solvent was added.
The response factor of component 2 (F_2) was calculated from Eq 33:

$$F_2 = \frac{m_2}{m_1}\frac{A_1}{A_2} \tag{33}$$

Therefore, the vapour or liquid composition of component 1 can be calculated from:

$$x_1 = \frac{\frac{A_1}{M_1}}{\frac{A_1}{M_1} + \left(F_2 \frac{A_2}{M_2} \right)} \tag{34}$$

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 are masses in the gravimetrically prepared sample of components 1 and 2, respectively. The maximum error of liquid and vapour composition measurements was estimated to be 0.001-mole fraction.

After the GC calibration was performed, the liquid and vapour samples were analysed with a HP 6850A gas chromatograph equipped with an auto sampler and a flame ionisation detector (FID). The GC column and the programs used depend on the systems to be analysed.

4.1.2.3.2 Refractometry

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 with an ABBEMAT-HP automatic refractometer. The measured refractive indexes of the calibration curves were fitted with a third-order polynomial. The compositions of the VLE liquid and vapour samples were determined from the calibration curves. The accuracy of the compositions using this procedure is estimated to be 0.001-mole fraction.

4.1.2.4 Consistency tests

The consistency test is used to analyse whether the measurements obey the thermodynamics relations. If the measurements do not fulfil the requirements then the measurements can be considered inconsistent. The infinite dilution and point tests are shown graphically in Figure 10 and Figure 11, respectively. The results of the thermodynamic consistency tests applied to all the sulphur-containing systems are summarised in Table 6.

4.1.2.4.1 Area test

The thermodynamic consistency test is based on the Gibbs-Duhem equation:

$$\frac{\Delta H}{RT^2} dT - \frac{\Delta V}{RT} dP + \sum_i x_i d \ln \gamma_i \tag{35}$$

The area consistency test [58] for isothermal condition is performed according to the equation:

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx = 0 \tag{36}$$

The values of $\ln \frac{\gamma_1}{\gamma_2}$ calculated from the experimental data points are plotted versus the mole fraction x_1. The data are considered consistent if the deviation between the integration areas above and below the x-axis (D) is less than 10%.

4.1.2.4.2 Infinite dilution test

The infinite dilution test [59] is carried out by the following equations

$$I_1 = 100 \left| I_1^* \right| < 30 \text{ and } I_2 = 100 \left| I_2^* \right| < 30 \tag{37 a\&b}$$

where

$$I_1^* = \frac{\left[\left(\frac{G^E/RT}{x_1 x_2}\right)_{x_1=0} - \ln\left(\frac{\gamma_1}{\gamma_2}\right)_{x_1=0}\right]}{\ln\left(\frac{\gamma_1}{\gamma_2}\right)_{x_1=0}}$$

and

$$I_2^* = \frac{\left[\left(\frac{G^E/RT}{x_1 x_2}\right)_{x_1=1} - \ln\left(\frac{\gamma_2}{\gamma_1}\right)_{x_1=1}\right]}{\ln\left(\frac{\gamma_2}{\gamma_1}\right)_{x_1=0}} \qquad \text{(38 a\&b)}$$

4.1.2.4.3 Point test

In the point test [58], the measurement set is considered to be consistent if the average deviations between the measured and calculated mole fractions of the vapour phase ($|\Delta y_{aver}|$) are smaller than 0.01.

4.2 Comparative Ebulliometry γ_i^∞ Measurements

4.2.1 Experimental setup

The comparative ebulliometer apparatus was built in the Helsinki University of Technology glass workshop. It is used for measuring the infinite dilution activity coefficient of sulphur compounds in hydrocarbons under isobaric conditions. The ebulliometers are placed in a close cupboard equipped with a ventilation system.

The equipment used for the determination of γ_i^∞ is shown schematically in Figure 9. The measurements were conducted with 4 Swietoslawski-type ebulliometers [35] in parallel, which allow the activity coefficients for several solutes to be determined simultaneously. The temperature differences between the ebulliometer containing pure solvent and those containing the mixtures were measured. 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 in the boiling temperatures at equilibrium were measured 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 the condenser at 277.15 K.

The ebulliometers were connected through liquid nitrogen traps to a pressure controller and ballast tank to a vacuum pump. A 50-dm^3 ballast tank is used to reduce pressure fluctuations and thus improve the pressure stability. The pressure was measured with a PMP 4070 pressure transducer (0-100 kPa) (Druck) equipped with a panel meter (Red Lion) with an accuracy of ± 0.15 kPa.

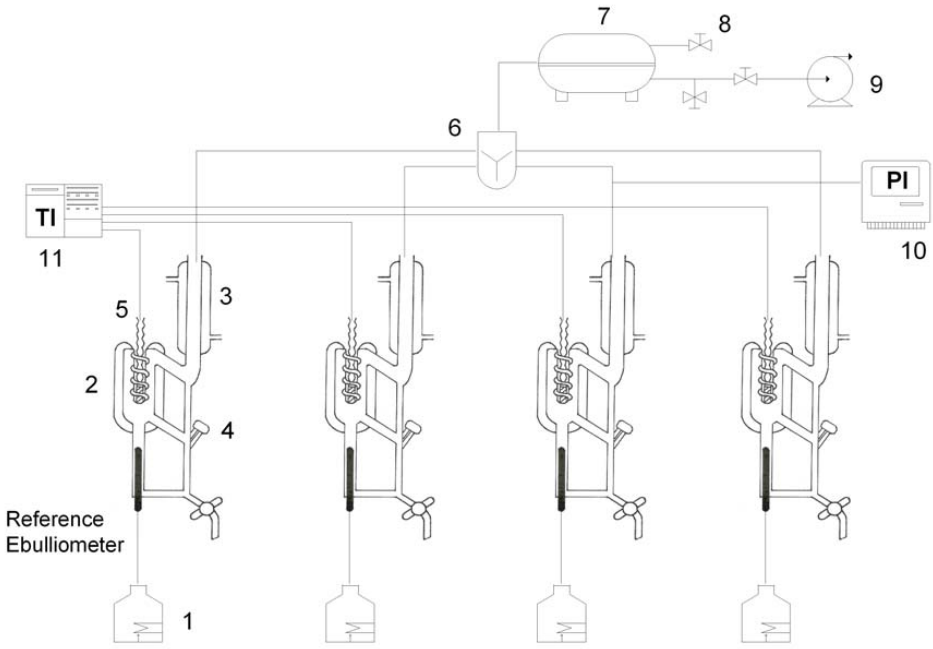

Figure 9 Overall design of system used to measure activity coefficients by comparative ebulliometers: (1) heating units, (2) equilibrium cell, (3) condenser, (4) injection port, (5) thermometer, (6) N_2 trap, (7) 50 dm^3 ballast, (8) manual valve, (9) vacuum pump, (10) pressure indicator, (11) temperature indicator.

4.2.2 Experimental procedures

Prior to the measurements, the ebulliometers were flushed with pure solvent and evacuated for 2 hours. As the measurements started, each ebulliometer was filled up with approximately 100 cm^3 of gravimetrically prepared pure solvent. The heating power was turned on and the cooling agent was circulated through the condenser. The system needed about 30-60 min to achieve a steady state. Once equilibrium was achieved, the vapour pressure of the solvent was measured and then compared to the literature values as a test of purity. Small amounts (typically about 0.05 ml) of different pure solutes were weighed in a gas-tight syringe (Hamilton Sample Lock) and injected into 3 ebulliometers. When equilibrium was achieved, the temperature differences between each ebulliometer and a reference ebulliometer were measured. The same amount of solute addition was repeated until 4 injections had been made in each loading ebulliometer. The total solute concentration in each ebulliometer was between 0.0025 and 0.0065 in mole fraction.

5 RESULTS AND DISCUSSIONS

5.1 Recirculation Still

The VLE measurements carried out with the recirculation still are presented in Table 3. The measurements of the systems 1-propanethiol, thiophene, and diethyl sulphide with toluene were carried out at 90.03 kPa [II]. The thiophene + *n*-hexane systems were measured at 323.15 K and 338.15 K and thiophene + 1-hexene systems were measured at 323.15 K and 333.15 K [III]. The diethyl sulphide + *n*-heptane and diethyl sulphide + 2,2,4-trimethylpentane systems were measured at 353.15 K and 363.15 K [IV]. The measurements of the diethyl sulphide + *n*-hexane systems were carried out at 323.15 K and 338.15 K and those of the diethyl sulphide + 1-hexene systems were carried out at 323.15 K and 333.15 K [V]. The diethyl sulphide + cyclohexane systems were measured at 343.15 K and 353.15 K and the diethyl sulphide + 2-ethoxy-2-methylpropane systems were measured at 333.15 K and 343.15 K [VI]. The measurements of the thiophene + 2,2,4-trimethylpentane systems were carried out at 343.15 K and 353.15 K and those of the thiophene + 2-ethoxy-2-methylpropane systems were carried out at 333.15 K and 343.15 K [VII].

The isobaric VLE measurements (liquid composition, vapour composition, temperature) and isothermal measurements (liquid composition, vapour composition, pressure), and calculated activity coefficients were tabulated and presented in graphs (for isothermal (P, x_1, and y_1), for isobaric (T, x_1, and y_1), and for activity coefficients (γ_1, γ_2, and x_1). The results were published in [II]-[VII].

5.1.1 Wilson interaction parameters

The experimental results were correlated with the Wilson model. The diethyl sulphide + *n*-heptane [IV], diethyl sulphide + *n*-hexane [V], and diethyl sulphide + cyclohexane [VI] systems were correlated with a Wilson temperature-dependent model obtained by simultaneously fitting the VLE and literature excess enthalpy (H^E) measurements by applying the appropriate objective function. The Wilson model gave satisfactory correlations for all systems. The Wilson interaction parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) are summarised in Table 5.

The Wilson temperature-dependent parameters (6 parameters) of the diethyl sulphide + 2,2,4-trimethylpentane [IV], diethyl sulphide + 1-hexene [V], and diethyl sulphide + 2-ethoxy-2-methylpropane [VI] systems were corrected and recorrelated to Wilson temperature-independent parameters (2 parameters) as presented in Table 5, because these systems were measured at only two temperatures, and thus the quadratic temperature dependence will overfit the data with parameters that should not be extrapolated.

Table 5. Results of Wilson interaction parameters (λ_{12} - λ_{11}) and (λ_{21} - λ_{22}): $\Delta\lambda_{12} = \lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}\left(\frac{T}{K}\right) + a_{2,12}\left(\frac{T}{K}\right)^2$ **and**

$\Delta\lambda_{21} = \lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}\left(\frac{T}{K}\right) + a_{2,21}\left(\frac{T}{K}\right)^2$

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}
1-propanethiol (1) + toluene (2) isobaric, P = 90.03 kPa	0	0	0	0	0	0
thiophene (1) + toluene (2) isobaric, P = 90.03 kPa	0	0	0	0	0	0
diethyl sulphide (1) + toluene (2) isobaric, P = 90.03 kPa	0	0	0	0	0	0
thiophene (1) + *n*-hexane (2) isothermal, T = 323.15 K	1516.417	0	0	1173.183	0	0
thiophene (1) + *n*-hexane (2) isothermal, T = 338.15 K	1407.728	0	0	1160.497	0	0
thiophene (1) + 1-hexene (2) isothermal, T = 323.15 K	1192.359	0	0	669.637	0	0
thiophene (1) + 1-hexene (2) isothermal, T = 333.15 K	1162.172	0	0	602.481	0	0
diethyl sulphide (1) + *n*-heptane (2) [a] isothermal, T = 353.15 K, 363.15 K	5746.383	-30.783	0.048	987.415	-0.325	-0.006
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K, 363.15 K	1126.793	0	0	6.625	0	0
diethyl sulphide (1) + *n*-hexane (2) [b] isothermal, T = 323.15 K, 338.15 K	5688.186	-31.061	0.051	969.830	1.139	-0.011
diethyl sulphide (1) + 1-hexene (2) isothermal, T = 323.15 K, 333.15 K	778.912	0	0	-133.132	0	0
diethyl sulphide (1) +cyclohexane (2) [c] isothermal, T = 343.15 K, 353.15 K	5874.918	-23.559	0.026	899.827	-7.862	0.016
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K, 343.15 K	214.632	0	0	260.000	0	0
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 343.15 K, 353.15 K	1751.129	0	0	1021.328	0	0
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K, 343.15 K	628.521	0	0	455.905	0	0

[a] VLE this work + H^E data from Ref [18].
[b] VLE this work + H^E data from Ref [19].
[c] VLE this work + H^E data from Ref [20].

5.1.2 Thermodynamic consistency tests

All the VLE measurements [I]-[VII] passed the integral, infinite dilution, and point tests. The results of thermodynamic consistency tests applied to all sulphur-containing systems [II]-[VII] are summarised in Table 6. For example, the infinite dilution and point tests for the 2-propanone (1) + 1,1-diethoxyethane (2) system at 323.15 K are shown in Figure 10 and Figure 11, respectively [I].

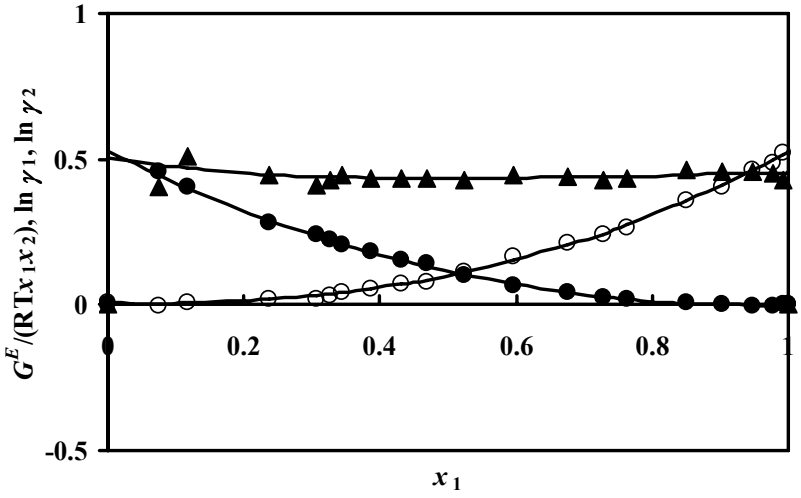

Figure 10 Infinite dilution test for the 2-propanone (1) + 1,1-diethoxyethane (2) system at 323.15 K: ▲, $G^E/(RTx_1x_2)$; ●, ln γ_1; ○, ln γ_2; —, Wilson model.

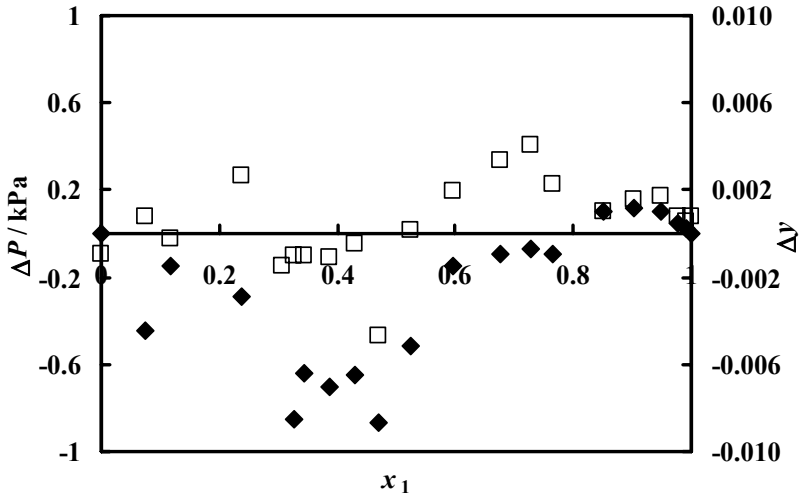

Figure 11 Point test for the 2-propanone (1) + 1,1-diethoxyethane (2) system at 323.15 K: ◆; Δ*y*, □; Δ*P* (Wilson model).

Table 6. Results of integral test, infinite dilution test; averages of absolute vapour fraction residuals (Δy_{aver}), averages of absolute temperature residuals (ΔT_{aver}), and averages of absolute pressure residuals (ΔP_{aver}) for the Wilson model, residual for UNIFAC, and residual for UNIFAC-Dortmund for the systems measured

system	integral test	infinite dilution test (%)		point test (Wilson)		residuals (original UNIFAC)		residuals (UNIFAC-Dortmund)	
	D %[d]	I_1^e x_1=0	I_2^e x_1=1	$\lvert\Delta y_{aver}\rvert$[f]	$\lvert\Delta P_{aver}\rvert$ (kPa)	$\lvert\Delta y_{aver}\rvert$	$\lvert\Delta P_{aver}\rvert$ (kPa)	$\lvert\Delta y_{aver}\rvert$	$\lvert\Delta P_{aver}\rvert$ (kPa)
1-propanethiol (1) + toluene (2) isobaric, P = 90.03 kPa	–	–	–	0.004	0.07 $\lvert\Delta T_{aver}\rvert$	0.019	1.63 $\lvert\Delta T_{aver}\rvert$	–	–
thiophene (1) + toluene (2) isobaric, P = 90.03 kPa	–	–	–	0.001	0.12 $\lvert\Delta T_{aver}\rvert$	0.011	0.80 $\lvert\Delta T_{aver}\rvert$	0.004	0.23 $\lvert\Delta T_{aver}\rvert$
diethyl sulphide (1) + toluene (2) isobaric, P = 90.03 kPa	–	–	–	0.001	0.08 $\lvert\Delta T_{aver}\rvert$	–	–	–	–
thiophene (1) + *n*-hexane (2) isothermal, T = 323.15 K	0.85	5.0	-4.9	0.001	0.07	0.007	0.77	0.013	1.28
thiophene (1) + *n*-hexane (2) isothermal, T = 338.15 K	0.02	-6.2	-5.7	0.002	0.15	0.004	0.44	0.022	4.09
thiophene (1) + 1-hexene (2) isothermal, T = 323.15 K	0.80	5.5	-13.4	0.001	0.07	–	–	–	–
thiophene (1) + 1-hexene (2) isothermal, T = 333.15 K	1.76	4.6	-7.9	0.002	0.13	–	–	–	–
diethyl sulphide (1) + *n*-heptane (2)[a] isothermal, T = 353.15 K	3.8	4.8	-7.1	0.001	0.07	0.006	0.95	–	–
diethyl sulphide (1) + *n*-heptane (2)[a] isothermal, T = 363.15 K	3.9	-3.4	-0.6	0.001	0.18	0.005	1.00	–	–
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	1.2	3.0	1.0	0.001	0.07	0.009	1.37	–	–
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 363.15 K	2.4	-10.5	-1.0	0.001	0.14	0.008	1.59	–	–
diethyl sulphide (1) + *n*-hexane (2)[b] isothermal, T = 323.15 K	0.1	-4.1	-21.7	0.001	0.06	0.011	0.70	–	–
diethyl sulphide (1) + *n*-hexane (2)[b] isothermal, T = 338.15 K	0.9	1.7	-27.0	0.001	0.15	0.010	1.24	–	–
diethyl sulphide (1) + 1-hexene (2) isothermal, T = 323.15 K	8.3	-12.0	0.2	0.002	0.12	–	–	–	–
diethyl sulphide (1) + 1-hexene (2) isothermal, T = 333.15 K	3.3	-3.4	-27.1	0.001	0.11	–	–	–	–
diethyl sulphide (1) + cyclohexane (2)[c] isothermal, T = 343.15 K	4.6	-2.7	-6.6	0.001	0.09	0.002	0.32	–	–
diethyl sulphide (1) + cyclohexane (2)[c] isothermal, T = 353.15 K	3.3	-5.1	-15.6	0.001	0.18	0.002	0.09	–	–
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	0.7	-12.5	-26.7	0.001	0.06	–	–	–	–
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	2.0	-27.9	-23.9	0.001	0.11	–	–	–	–
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 343.15 K	2.1	15.8	4.5	0.006	0.23	0.007	0.98	0.007	0.61

Table 6. ***(continued)***

thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	1.2	3.8	5.8	0.002	0.09	0.005	0.91	0.011	2.06
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	1.0	-6.0	-7.4	0.001	0.07	–	–	–	–
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	2.4	-7.7	-13.8	0.001	0.08	–	–	–	–

(–) not available
[a]VLE this work + H^E data from Ref [18].
[b]VLE this work + H^E data from Ref [19].
[c]VLE this work + H^E data from Ref [20].

The criterion for passing the test:
[d] $D < 10\%$ [58].
[e] $I_1 = 100\left|I_1^*\right| < 30$ and $I_2 = 100\left|I_2^*\right| < 30$ [59].
[f] $\left|\Delta y_{aver}\right| < 0.01$ [58].

5.1.3 γ^∞ of sulphur compounds in hydrocarbons

The VLE measurements were compared with the VLE prediction from the original UNIFAC, UNIFAC-Dortmund, and COSMO-RS predictive models. The compositions, pressures, and temperatures of the azeotropes, together with the activity coefficients at infinite dilution (γ^∞) from experimental results and from predictive models, are summarised in Table 7.

Table 7. Activity coefficients at infinite dilution, γ^∞, and azeotropic composition (x_{1az}, T_{az}, P_{az}) for systems measured; Methods: A, measured; B, extrapolation from experimental VLE with the Wilson model; C, original UNIFAC; D, UNIFAC-Dortmund; E, COSMO-RS

system	γ_1^∞	γ_2^∞	x_{1az}	T_{az} (K)	P_{az} (kPa)	method
1-propanethiol (1) + toluene (2) isobaric, P = 90.03 kPa	1.04	1.06	–	–	–	B
thiophene (1) + 1-hexene (2) isothermal, T = 323.15 K	1.63	2.0	–	–	–	B
thiophene (1) + 1-hexene (2) isothermal, T = 333.15 K	1.57	1.89	–	–	–	B
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	1.21 1.44	1.40 1.88	– –	– –	– –	B E
thiophene (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	1.20 1.43	1.38 1.84	– –	– –	– –	B E

Table 7. ***(continued)***

system	γ_1^∞	γ_2^∞	x_{1az}	T_{az} (K)	P_{az} (kPa)	method
thiophene (1) + toluene (2) isobaric, P = 90.03 kPa	1.00	1.03	–	–	–	B
thiophene (1) + *n*-hexane (2) isothermal, T = 323.15 K	–	–	0.117	323.15	54.75	A
	1.96	2.71	0.122	323.15	54.66	B
	2.15	3.36	0.197	323.15	55.57	D
thiophene (1) + *n*-hexane (2) isothermal, T = 338.15 K	–	–	0.110	338.15	90.68	A
	1.82	2.49	0.111	338.15	90.90	B
	1.73	2.40	0.063	338.15	90.77	C
	2.18	3.61	0.248	338.15	94.11	D
	–	–	0.113	341.61	101.32	Ref [22]
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 343.15 K	–	–	0.816	343.15	67.76	A
	1.72	2.62	0.820	343.15	67.35	B
	1.53	2.59	0.843	343.15	66.93	C
	1.68	3.34	0.812	343.15	68.87	D
	2.68	4.77	0.728	343.15	74.29	E
thiophene (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	–	–	0.826	353.15	93.30	A
	1.68	2.54	0.822	353.15	93.20	B
	1.50	2.52	0.845	353.15	92.66	C
	1.71	3.55	0.801	353.15	96.57	D
	2.56	4.43	0.733	353.15	101.90	E
diethyl sulphide (1) + *n*-hexane (2) [c] **isothermal, T = 323.15 K**	1.51	1.55	–	–	–	B
diethyl sulphide (1) + *n*-hexane (2) [c] **isothermal, T = 338.15 K**	1.47	1.49	–	–	–	B
diethyl sulphide (1) + 1-hexene (2) isothermal, T = 323.15 K	1.27	1.26	–	–	–	B
diethyl sulphide (1) + 1-hexene (2) isothermal, T = 333.15 K	1.26	1.25	–	–	–	B
diethyl sulphide (1) + cyclohexane (2) [d] **isothermal, T = 343.15 K**	1.38	1.34	–	–	–	B
diethyl sulphide (1) + cyclohexane (2) [d] **isothermal, T = 353.15 K**	1.36	1.32	–	–	–	B
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 333.15 K	1.13	1.17	–	–	–	B

Table 7. ***(continued)***

system	γ_1^∞	γ_2^∞	x_{1az}	T_{az} (K)	P_{az} (kPa)	method
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) isothermal, T = 343.15 K	1.13	1.17	–	–	–	B
diethyl sulphide (1) + toluene (2) isobaric, P = 90.03 kPa	1.00	1.00	–	–	–	B
diethyl sulphide (1) + *n*-heptane (2) [a] **isothermal, T = 353.15 K**	–	–	0.791	353.15	71.15	A
	1.34	1.42	0.805	353.15	71.17	B
	1.45	1.50	0.782	353.15	71.78	E
	1.24	1.30	0.896	353.15	70.39	C
diethyl sulphide (1) + *n*-heptane (2)[a] **isothermal, T = 363.15 K**	–	–	0.797	363.15	97.28	A
	1.33	1.40	0.800	363.15	97.47	B
	1.43	1.48	0.782	363.15	98.19	E
	1.23	1.29	0.890	363.15	96.39	C
	–	–	0.798	< 364.95	101.32	Ref [23]
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 353.15 K	–	–	0.782	353.15	71.43	A
	1.36	1.47	0.791	353.15	71.52	B
	1.48	1.55	0.763	353.15	72.12	E
	1.19	1.28	0.930	353.15	70.26	C
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) isothermal, T = 363.15 K	–	–	0.798	363.15	97.47	A
	1.34	1.45	0.805	363.15	97.60	B
	1.46	1.52	0.777	363.15	98.35	E
	1.18	1.27	0.941	363.15	96.15	C
	–	–	0.809	364.59	101.32	Ref [22]

(–) none

The activity coefficients at infinite dilution (γ^∞) were extrapolated from the VLE measurements with the Wilson model for the following systems: 1-propanethiol in toluene; thiophene in toluene, *n*-hexane, 1-hexene, 2,2,4-trimethylpentane, and 2-ethoxy-2-methylpropane; diethyl sulphide in toluene, *n*-heptane, 2,2,4-trimethylpentane, *n*-hexane, 1-hexene, cyclohexane, and 2-ethoxy-2-methylpropane. All the measured γ^∞ of sulphur compounds in hydrocarbons are less than two. The 1-propanethiol, thiophene, and diethyl sulphide in toluene show ideal behaviour, and thus the γ^∞ for these systems are one.

As shown in Figure 12 and Figure 13, the γ^∞ values of thiophene in *n*-hexane, 1-hexene, 2-ethoxy-2-methylpropane, and 2,2,4-trimethylpentane decrease with increasing temperature, as do the γ^∞ values of diethyl sulphide in *n*-hexane, 1-hexene, cyclohexane, and 2-ethoxy-2-methylpropane, *n*-heptane, and 2,2,4-trimethylpentane. The γ^∞ values of thiophene and diethyl sulphide in hydrocarbons also decrease with an increase in the number of C-atoms of

the alkanes. These positive deviations from Raoult's law become smaller with increasing temperature and alkane chain length.

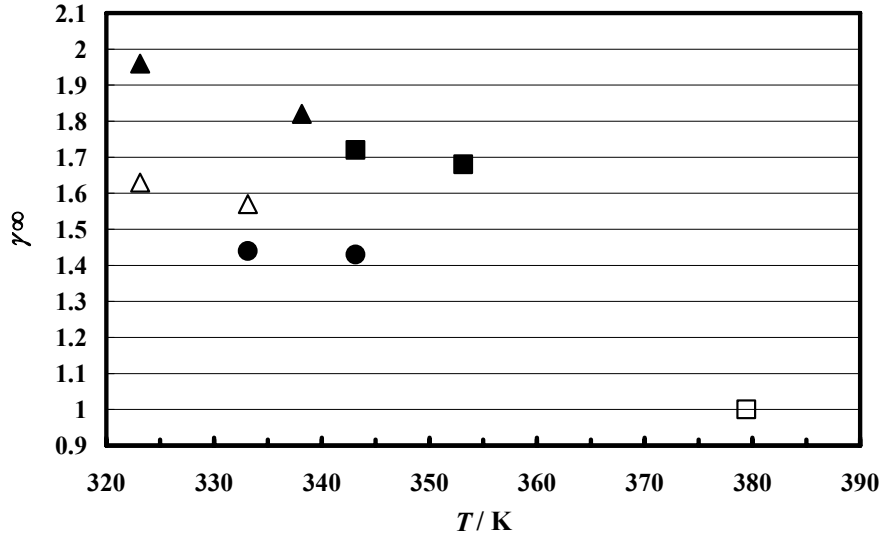

Figure 12 γ^{∞} of thiophene in various hydrocarbons obtained from regression of experimental VLE with the Wilson model: ▲, *n*-hexane; Δ, 1-hexene; ●, 2-ethoxy-2-methylpropane; □, toluene, ■, 2,2,4-trimethylpentane

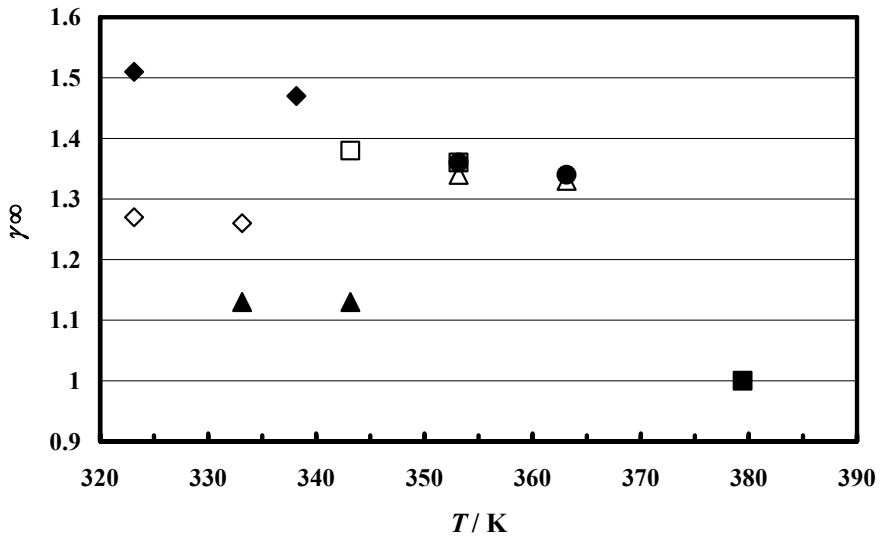

Figure 13 γ^{∞} of diethyl sulphide in various hydrocarbons obtained from regression of experimental VLE with the Wilson model: ♦, *n*-hexane; ◊, 1-hexene; ▲, 2-ethoxy-2-methylpropane; □, cyclohexane, ■, toluene; Δ, *n*-heptane; ●, 2,2,4-trimethylpentane

5.1.4 Azeotropy and ideality

Azeotropy behaviour and ideality of sulphur compounds in hydrocarbons of the system measured is presented in Table 8. The systems 1-propanethiol, thiophene, and diethyl sulphide in toluene show nearly ideal behaviour, as shown in Figure 5, Figure 6, and Figure 7, respectively. No azeotropes were found in these systems. Since sulphur compounds (sulphides, mercaptans, and thiophenes) and toluene have no hydrogen bond-forming capabilities, the mixture of those compounds forms ideal mixtures.

No azeotrope formation was observed for the systems thiophene + 1-hexene and diethyl sulphide + 1-hexene. The measurement of the 1-propanethiol + 1-hexene system was attempted. A reaction between thiol and alkene was observed.

The systems thiophene + 1-hexene and thiophene + 2-ethoxy-2-methylpropane, as well as systems of diethyl sulphide with *n*-hexane, 1-hexene, cyclohexane, 2-ethoxy-2-methylpropane, show positive deviation and strong nonideality. No azeotropes formed in these systems, as a result of the large difference in the boiling points of the pure components.

The systems thiophene (T_b=357.31 K) + *n*-hexane (T_b=341.88 K) and thiophene + 2,2,4-trimethylpentane (T_b=372.39 K), as well as systems diethyl sulphide (T_b=365.25 K) + *n*-heptane (T_b=371.58 K), and diethyl sulphide + 2,2,4-trimethylpentane show positive deviations from Raoult's law. These systems exhibit maximum pressure azeotropy. The azeotrope forms when the boiling points of the pure components are very close. The closer the boiling points of the pure components and the less ideal the mixture, the greater the likelihood of an azeotrope.

If there is a point in the composition space in which the vapour pressures of the two components are equal at a given temperature (in the region of the normal boiling points of the pure components), this may correspond to an azeotropic point which is called a Bancroft point. A Bancroft point occurred at about 230 K for the 2-propanol + 1,1-diethoxyethane system when each vapour pressure was extrapolated to a lower temperature by the Antoine parameters. The azeotropic behavior with a minimum boiling temperature was observed at T = 353.15 K, P = 94.2 kPa, x_1= 0.916 ± 0.005.

Table 8. Azeotropy and ideality of sulphur compounds in hydrocarbon of the systems measured

system	azeotropy	Raoult's law
1-propanethiol (1) + toluene (2) **isobaric, P = 90.03 kPa**	none	nearly ideal
thiophene (1) + 1-hexene (2) **isothermal, T = 323.15 K, 333.15 K**	none	positive deviation
thiophene (1) + 2-ethoxy-2-methylpropane (2) **isothermal, T = 333.15 K, 343.15 K**	none	positive deviation
thiophene (1) + toluene (2) **isobaric, P = 90.03 kPa**	none	nearly ideal

Table 8. ***(continued)***

system	azeotropy	Raoult's law
thiophene (1) + *n*-hexane (2) **isothermal, T = 323.15 K, 338.15 K**	maximum pressure	positive deviation
thiophene (1) + 2,2,4-trimethylpentane (2) **isothermal, T = 343.15 K, 353.15 K**	maximum pressure	positive deviation
diethyl sulphide (1) + *n*-hexane (2) **isothermal, T = 323.15 K, 338.15 K**	none	positive deviation
diethyl sulphide (1) + 1-hexene (2) **isothermal, T = 323.15 K, 333.15 K**	none	positive deviation
diethyl sulphide (1) + cyclohexane (2) **isothermal, T = 343.15 K, 353.15 K**	none	positive deviation
diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) **isothermal, T = 333.15 K, 343.15 K**	none	positive deviation
diethyl sulphide (1) + toluene (2) **isobaric, P = 90.03 kPa**	none	nearly ideal
diethyl sulphide (1) + *n*-heptane (2) **isothermal, T = 353.15 K, 363.15 K**	maximum pressure	positive deviation
diethyl sulphide (1) + 2,2,4-trimethylpentane (2) **isothermal, T = 353.15 K, 363.15 K**	maximum pressure	positive deviation

5.1.5 Estimation methods

Thiols, sulphides, and thiophenes are the major impurities present in crude oils and are also found in distillates and in products from cracking, coking, and alkylation processes. Therefore the isobaric vapour-liquid equilibria for a binary system of 1-propanethiol, thiophene, and diethyl sulphide with toluene at 90.03 kPa were measured [II]. The original UNIFAC interaction parameters for sulphides (CH_2S) and toluene ($AC\text{-}CH_2$) functional group are not available; hence no original UNIFAC prediction for the diethyl sulphide + toluene system is possible. As can be seen from Figure 7, the prediction of COSMO-RS is close to the experimental results. In Figure 5, the original UNIFAC and COSMO-RS predictions for the 1-propanethiol + toluene system are comparable, even though they do not match well with the experiments. The thiophene + toluene system was predicted using the UNIFAC-Dortmund and COSMO-RS models. From Figure 6, it can be seen that the predictions with COSMO-RS are slightly better when compared to UNIFAC-Dortmund, while the original UNIFAC gave unsatisfactory results. For the sulphur-containing systems, the modification of the COSMO-RS model by the exclusion of the van der Waals interaction from the binary surface interaction energy improves the quality of the prediction. The results of the prediction of our VLE systems with the modified COSMO-RS are shown in Figure 5, Figure 6, and Figure 7.

Thiophene and its derivatives contribute to the overall sulphur content of a particular fraction and to the amount of corrosive sulphur oxides formed during combustion. Thus, isothermal vapour-liquid equilibria for the binary systems thiophene + *n*-hexane at 323.15 K and 338.15 K, thiophene + 1-hexene at 323.15 K and 333.15 K [III], thiophene + 2,2,4-trimethylpentane at 343.15 K and 353.15 K, and thiophene + 2-ethoxy-2-methylpropane at 333.15 K and 343.15 K [VII] were measured.

Thiophene + *n*-hexane systems at 323.15 K and 338.15 K were predicted with the original UNIFAC, UNIFAC-Dortmund, and COSMO-RS, which are shown in Figure 14 and Figure 15, respectively.

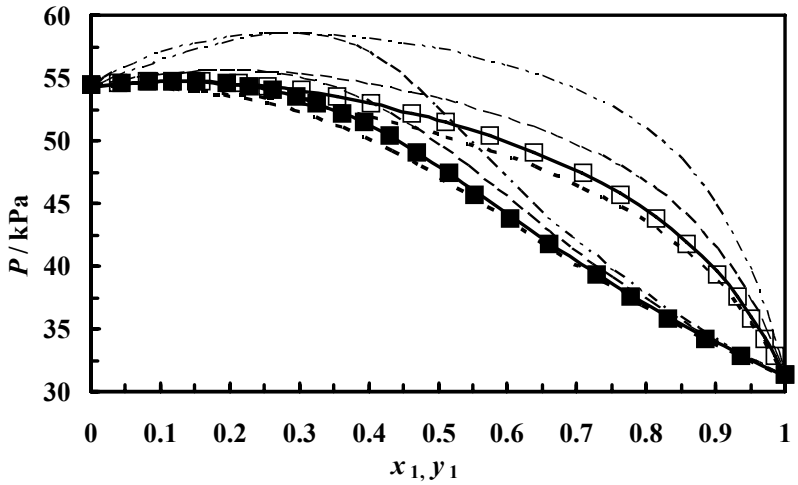

Figure 14 Pressure–composition diagram for the thiophene (1) + *n*-hexane (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC; – –, UNIFAC–Dortmund; – - - –, COSMO-RS.

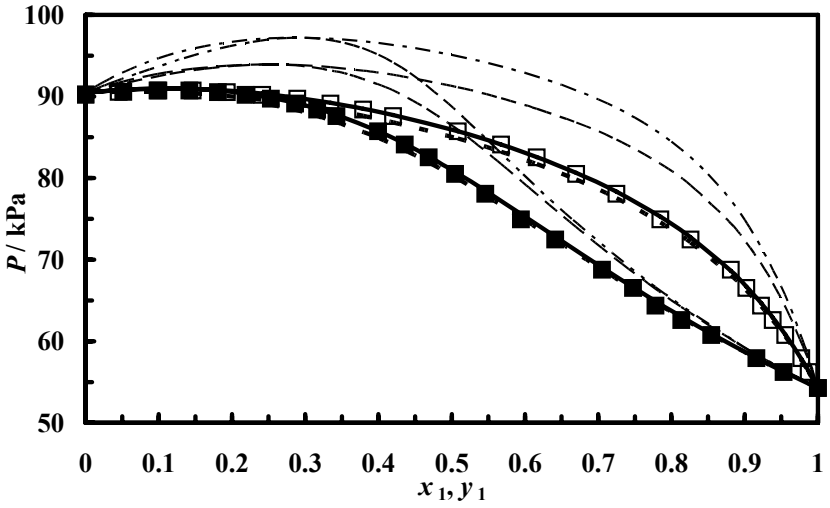

Figure 15 Pressure–composition diagram for the thiophene (1) + *n*-hexane (2) system at 338.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC; – –, UNIFAC–Dortmund; – - - –, COSMO-RS.

The original UNIFAC shows a better prediction for the system at 338.15 K compared to the prediction for the system at 323.15 K, whereas UNIFAC-Dortmund and COSMO-RS gave unsatisfactory predictions for both systems. The activity coefficient-composition diagram for the thiophene + *n*-hexane system at 338.15 K is presented in Figure 16.

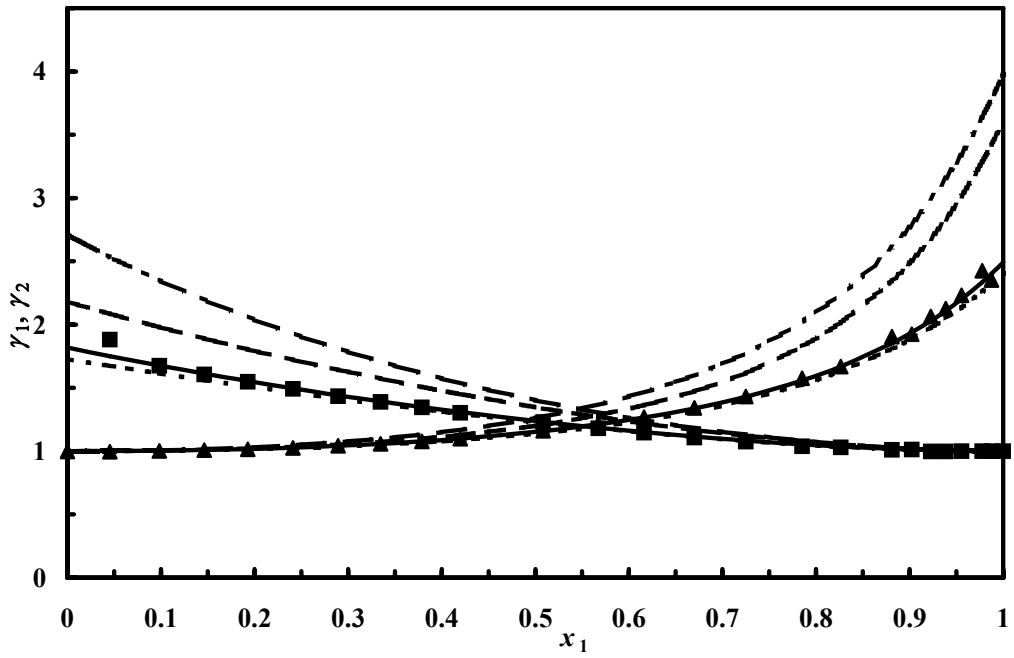

Figure 16 Activity coefficient–composition diagram for the thiophene (1) + *n*-hexane (2) system at 338.15 K: ■, γ_1 from the data; ▲, γ_2 from the data; —, γ_1 and γ_2 from Wilson model; - - -, γ_1 and γ_2 from original UNIFAC; – –, from UNIFAC–Dortmund; – - –, from COSMO-RS.

The original UNIFAC and UNIFAC-Dortmund interaction parameter for thiophene (C_4H_4S functional group) and 1-hexene (CH_2=CH functional group) is not available; hence no original UNIFAC and UNIFAC-Dortmund prediction for the thiophene + 1-hexene system is possible. As can be seen from Figure 17, the COSMO-RS prediction for the thiophene + 1-hexene system at 323.15 K is close to the experimental results.

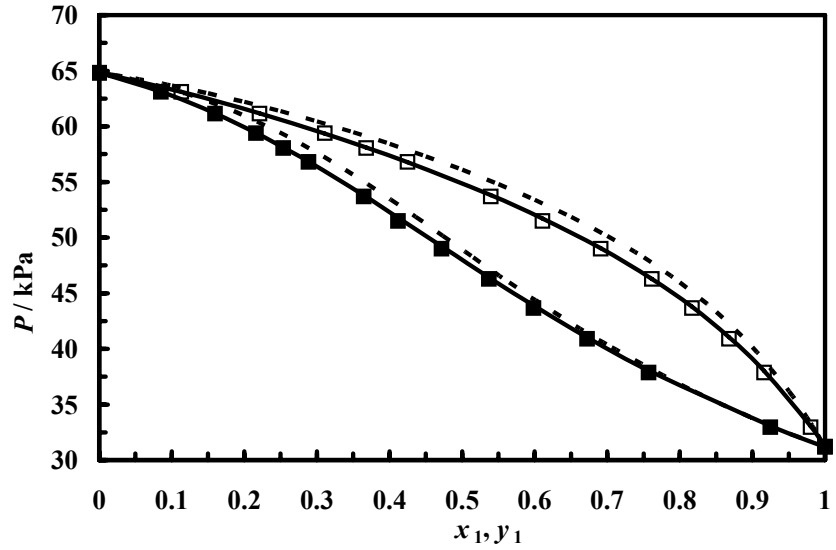

Figure 17 Pressure–composition diagram for the thiophene (1) + 1-hexene (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, COSMO-RS.

The thiophene + 2,2,4-trimethylpentane system at 343.15 K and 353.15 K were predicted with the original UNIFAC, UNIFAC-Dortmund, and COSMO-RS, which are presented in Figure 18 and Figure 19, respectively.

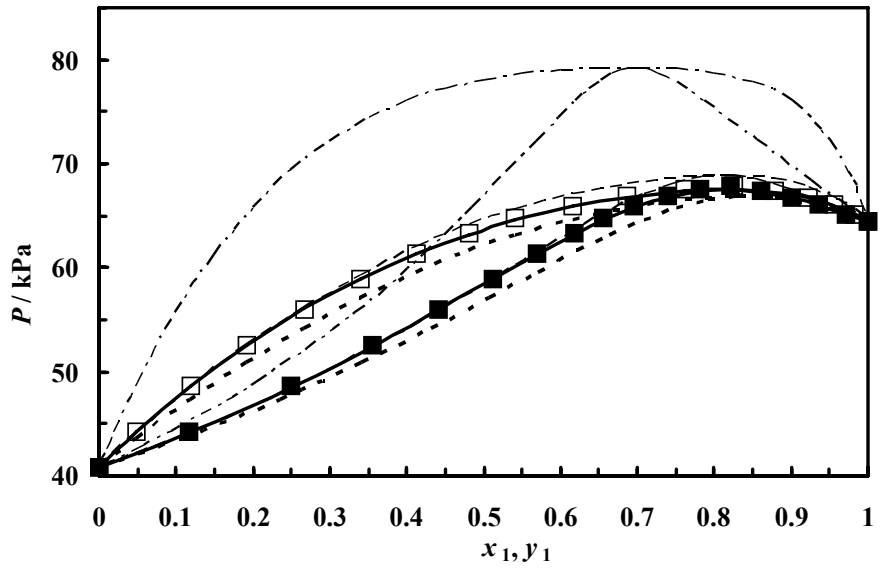

Figure 18 Pressure–composition diagram for the thiophene (1) + 2,2,4-trimethylpentane (2) system at 343.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC; – –, UNIFAC-Dortmund; — - —, COSMO-RS.

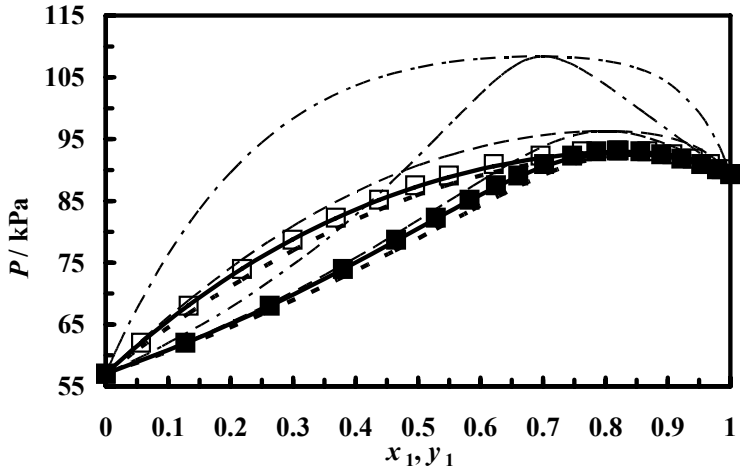

Figure 19 Pressure–composition diagram for the thiophene (1) + 2,2,4-trimethylpentane (2) system at 353.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC; – –, UNIFAC-Dortmund; — - —, COSMO-RS.

The original UNIFAC gave good agreement for the thiophene + 2,2,4-trimethylpentane system at 353.15 K, while UNIFAC-Dortmund gave better agreement than the original UNIFAC for the thiophene + 2,2,4-trimethylpentane system at 343.15 K. COSMO-RS shows poor prediction for these systems at both temperatures.

The original UNIFAC interaction parameter for the thiophene (C_4H_4S functional group) and 2-ethoxy-2-methylpropane (CH_2O functional group) system is not available; hence no original UNIFAC prediction is possible for the thiophene + 2-ethoxy-2-methylpropane system. As can be seen from Figure 20, the COSMO-RS gave poor prediction for the thiophene + 2-ethoxy-2-methylpropane system at 333.15 K.

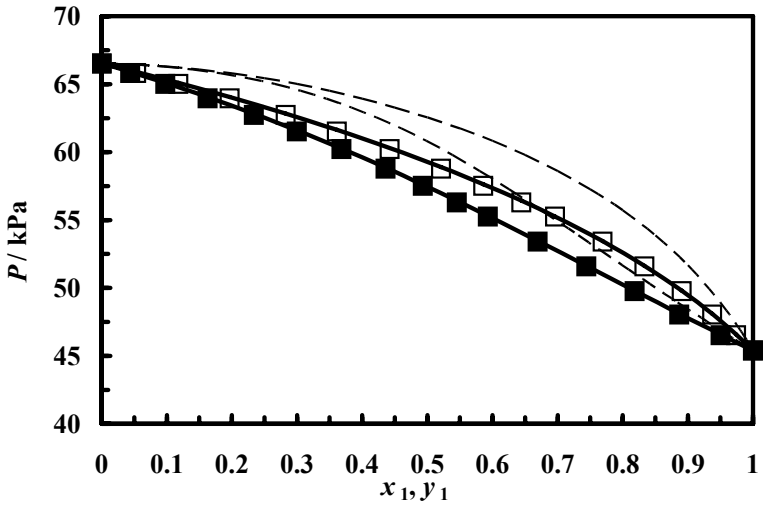

Figure 20 Pressure–composition diagram for the thiophene (1) + 2-ethoxy-2-methylpropane (2) system at 333.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; – –, COSMO-RS.

Diethyl sulphide is one of the common organic sulphides found in lower-boiling distillates. Hence, in this work isothermal vapour-liquid equilibria for the binary system of diethyl sulphide + *n*-heptane and diethyl sulphide + 2,2,4-trimethylpentane were measured at 353.15 K and 363.15 K [IV], diethyl sulphide + *n*-hexane were measured at 323.15 K and 338.15 K, diethyl sulphide + 1-hexene were measured at 323.15 K and 333.15 K [V], diethyl sulphide + cyclohexane were measured at 343.15 K and 353.15 K, and diethyl sulphide + 2-ethoxy-2-methylpropane were measured at 333.15 K and 343.15 K [VI].

The measured VLE of diethyl sulphide + *n*-heptane systems were used simultaneously with the excess enthalpy from the literature for a correlation of temperature-dependent Wilson parameters. These parameters were used in the calculation to describe the systems. The measurements of the diethyl sulphide + *n*-heptane system were predicted with the original UNIFAC and COSMO-RS. The VLE results of the diethyl sulphide + *n*-heptane system at 363.15 K are presented in Figure 21. The original UNIFAC and COSMO-RS give unsatisfactory predictions for the systems measured.

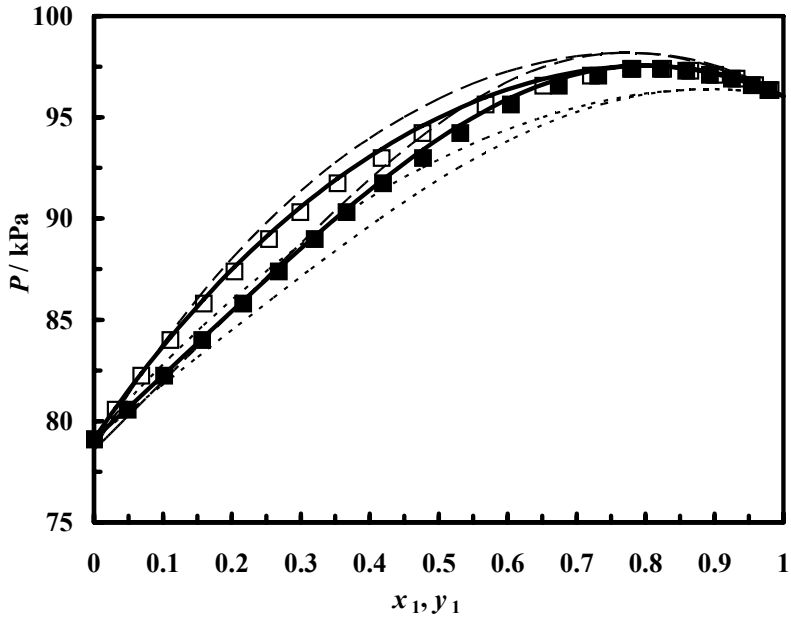

Figure 21 Pressure–composition diagram for the diethyl sulphide (1) + *n*-heptane (2) system at 363.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data; - - -, original UNIFAC; – –, COSMO-RS.

The measurements of the diethyl sulphide + 2,2,4-trimethylpentane system were predicted with the original UNIFAC and COSMO-RS. The results of the diethyl sulphide + 2,2,4-trimethylpentane system at 353.15 K are presented in Figure 22. The original UNIFAC and COSMO-RS give unsatisfactory predictions for this system.

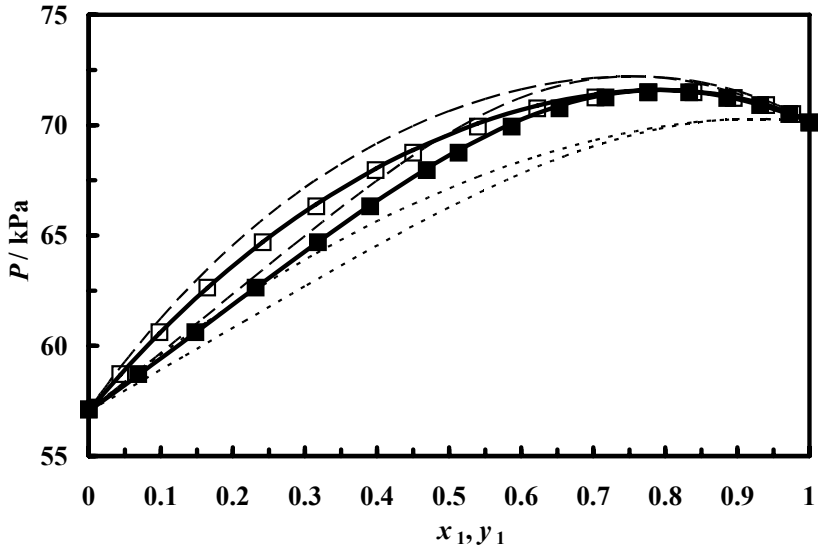

Figure 22 Pressure–composition diagram for the diethyl sulphide (1) + 2,2,4-trimethylpentane (2) system at 353.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson model-extended data; - - -, original UNIFAC; – –, COSMO-RS.

The measurements for the diethyl sulphide + *n*-hexane system were predicted with the original UNIFAC and COSMO-RS. The results of the diethyl sulphide + *n*-hexane system at 323.15 K are presented in Figure 23. The COSMO-RS predictions are quite close to the experimental results and show better prediction compared to the original UNIFAC.

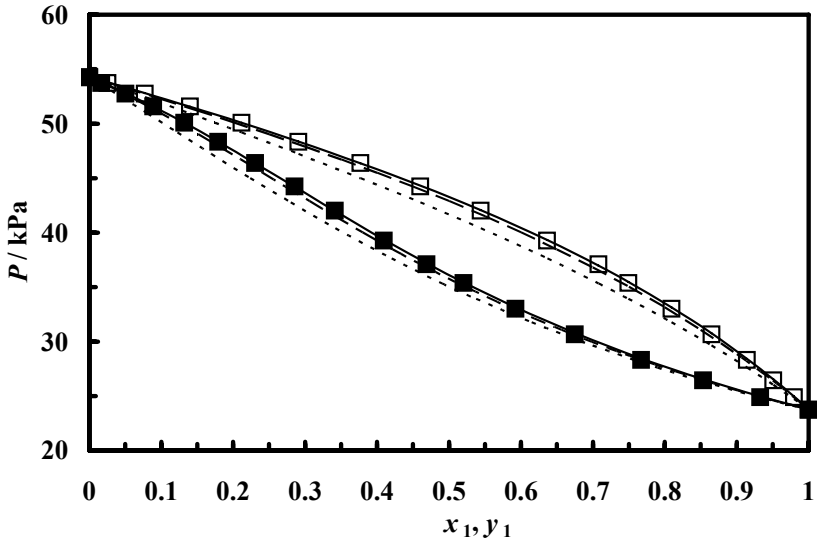

Figure 23 Pressure–composition diagram for the diethyl sulphide (1) + *n*-hexane (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC; – –, COSMO-RS.

The measurements of the diethyl sulphide + 1-hexene systems were predicted with COSMO-RS. COSMO-RS gives poor prediction for these systems. The results for the diethyl sulphide + 1-hexene system at 323.15 K are presented in Figure 24. The original UNIFAC interaction parameter for the diethyl sulphide (CH_2S functional group) and 1-hexene (CH_2=CH functional group) is not available; hence no original UNIFAC prediction is possible for the diethyl sulphide + 1-hexene system.

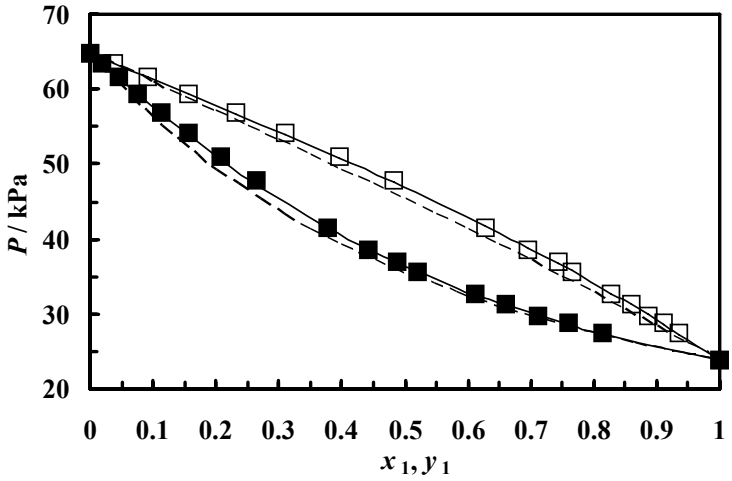

Figure 24 Pressure–composition diagram for the diethyl sulphide (1) + 1-hexene (2) system at 323.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; – –, COSMO-RS.

The measurements for the diethyl sulphide + cyclohexane system were predicted with the original UNIFAC model and COSMO-RS. The results for the diethyl sulphide + cyclohexane system at 343.15 K are presented in Figure 25. The original UNIFAC predictions are quite close to the experimental results, while COSMO-RS shows less accurate prediction for these systems.

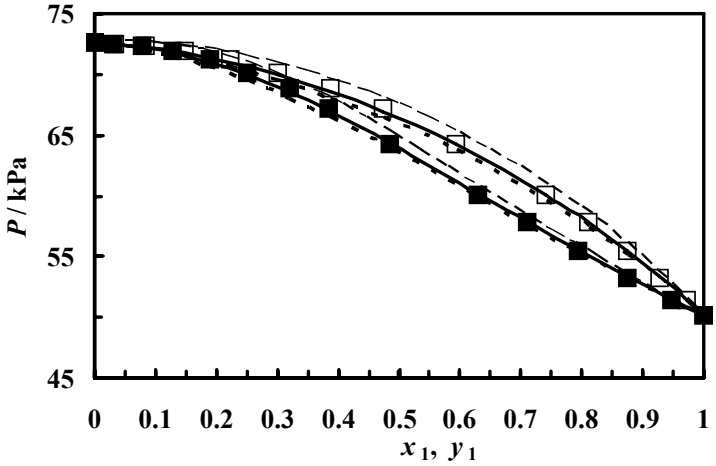

Figure 25 Pressure–composition diagram for the diethyl sulphide (1) + cyclohexane (2) system at 343.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; - - -, UNIFAC; – –, COSMO-RS.

The original UNIFAC interaction parameter for the diethyl sulphide (CH_2S functional group) and 2-ethoxy-2-methylpropane (CH_2O functional group) is not available; hence no original UNIFAC prediction is possible for the diethyl sulphide + 2-ethoxy-2-methylpropane system. As can be seen from Figure 26, COSMO-RS also gives poor prediction for these systems.

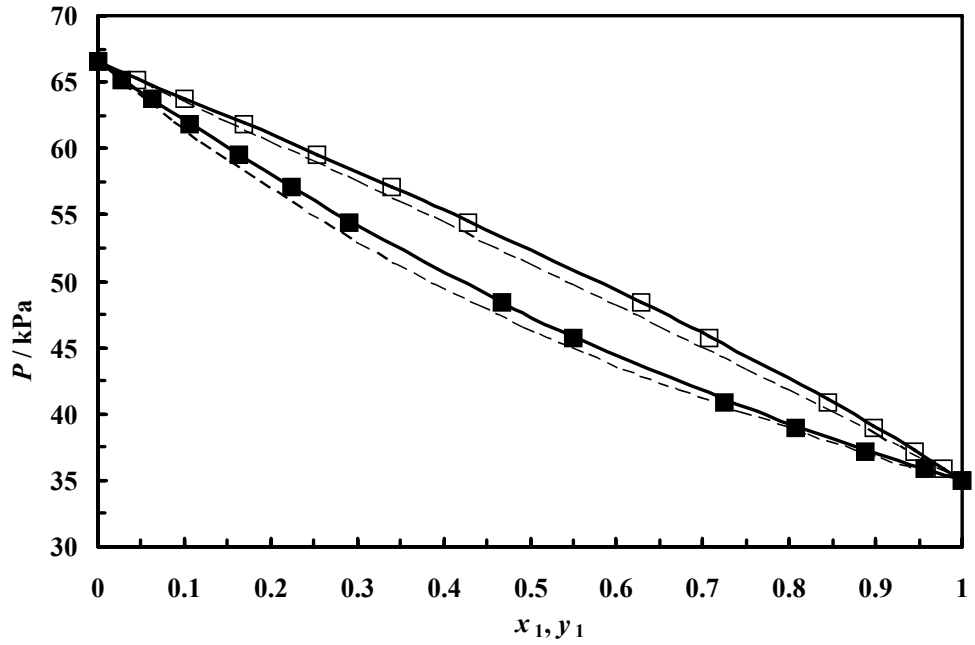

Figure 26 Pressure–composition diagram for the diethyl sulphide (1) + 2-ethoxy-2-methylpropane (2) system at 333.15 K: □, x_1 measured; ■, y_1 measured; —, Wilson; – –, COSMO-RS.

Ethanol is already being used extensively as a fuel additive and the use of ethanol fuel alone (biofuel) or as part of a mix with gasoline is increasing. One way to produce ethanol is through fermentation. Ethanol is purified by azeotropic distillation and dehydration in order to obtain nearly pure ethanol with a purity of 99.5 to 99.9%. However, a small amount of side products can be produced during the fermentation process, such as acetaldehyde, 2-propanol, ethyl ethanoate, and 1,1-diethoxyethane. Acetaldehyde will react with ethanol to form 1,1-diethoxyethane. Thus, in this work isothermal vapour-liquid equilibria for binary systems of 2-propanol + 1,1-diethoxyethane at 353.15 K, ethyl ethanoate + 1,1-diethoxyethane at 348.15 K, and 2-propanone + 1,1-diethoxyethane at 328.15 K were measured [I].

The measured isothermal equilibrium data for the 2-propanol + 1,1-diethoxyethane system at 353.15 K is presented in Figure 27. This system exhibits positive deviations from Raoult's law. Azeotropic behaviour with a minimum boiling temperature was observed at T = 353.15 K, P = 94.2 kPa, x_1 = 0.916 ± 0.005. The original UNIFAC gave good prediction for the system measured.

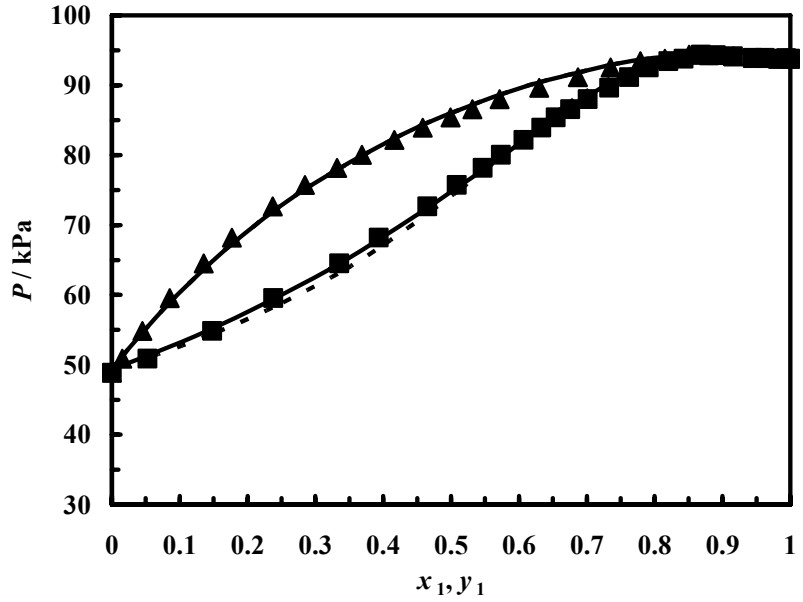

Figure 27 Pressure–composition diagram for the 2-propanol (1) + 1,1-diethoxyethane (2) system at 353.15 K: ▲, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC.

The measured isothermal equilibrium data for the 2-propanone + 1,1-diethoxyethane system at 328.15 K is presented in Figure 28. This system exhibits positive deviations from Raoult's law. No azeotropic behaviour was observed. The original UNIFAC gave good prediction for the system measured.

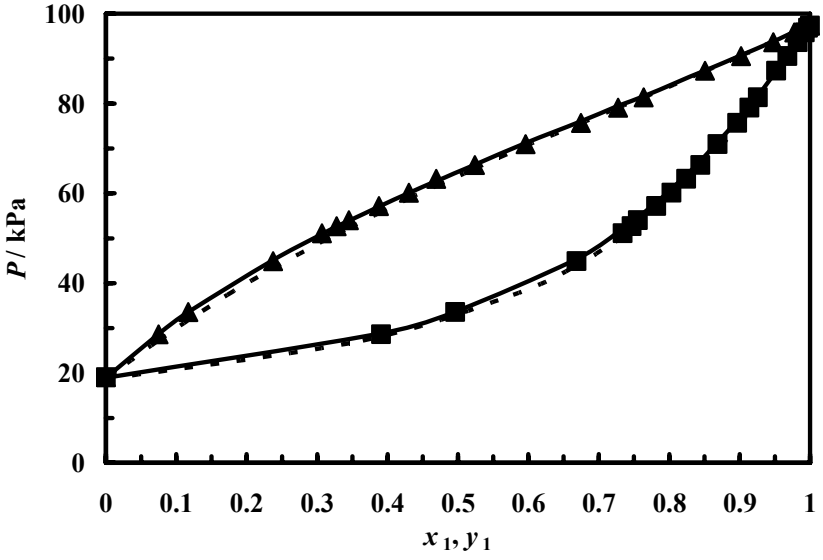

Figure 28 Pressure–composition diagram for the 2-propanone (1) + 1,1-diethoxyethane (2) system at 328.15 K: ▲, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC.

The measured isothermal equilibrium data for the ethyl ethanoate + 1,1-diethoxyethane system at 348.15 K is presented in Figure 29. This system exhibits positive deviations from Raoult's law. No azeotropic behaviour was observed. The original UNIFAC gave good prediction for the system measured.

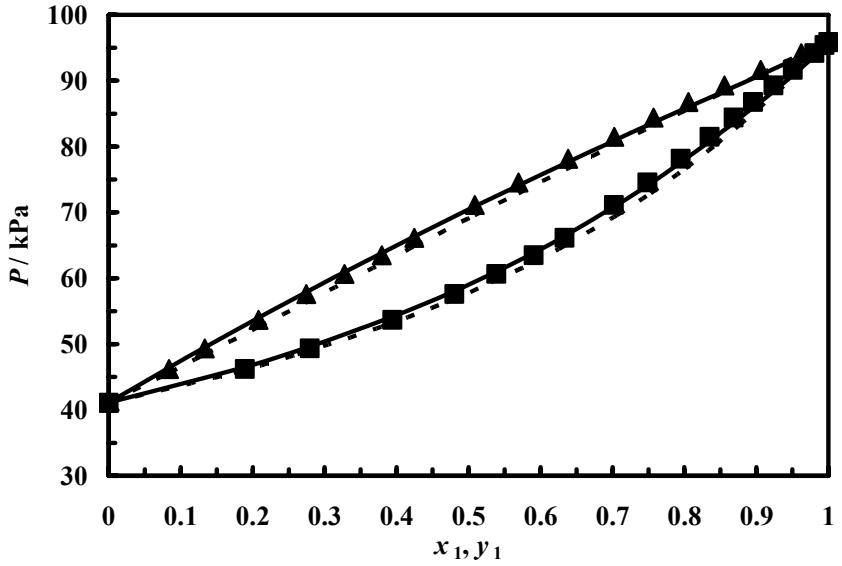

Figure 29 Pressure–composition diagram for the ethyl ethanoate (1) + 1,1-diethoxyethane (2) system at 348.15 K: ▲, x_1 measured; ■, y_1 measured; —, Wilson; - - -, original UNIFAC.

5.2 Differential Ebulliometry

5.2.1 Systems tested

Before sulphur component measurements were carried out, the reliability of the system was tested. First, the apparatus was used for taking water vapour pressure measurements in the range 30-90 kPa. The measurement results were compared to the literature correlation [41]. The difference of each ebulliometer was approximately 0.2 kPa.

Second, the apparatus was used to determine infinite dilution for an alcohol-water mixture. Measurements of infinite dilution for 2-propanol (1) + water (2) and ethanol (1) + water (2) mixtures were made at 4 different temperatures between 330.15 K and 370.15 K (pressure 17.7, 30, 50, and 90 kPa). The experimental results were compared to the literature data and predictive UNIFAC and also fitted to the Wilson model calculated by VLEFIT.

5.2.2 Sulphur component-hydrocarbon mixtures

Prior to the measurements, the vapour pressure of the solvent was measured and compared to the literature values, and then the Antoine coefficients were regressed.

An evaporation factor (*f*) is needed to calculate concentration in the equilibrium and is also used to determine the ebulliometric constant. The evaporation factor was determined from *n*-

hexane (1) + ethyl acetate (2) experiments at 74.018 kPa, 340.15 K at different compositions. The average *f* value is 0.055, which agreed well with Raal's result [50].

One example of typical results of measurements, equilibrium compositions, and determination of the limiting slope is shown in Figure 30.

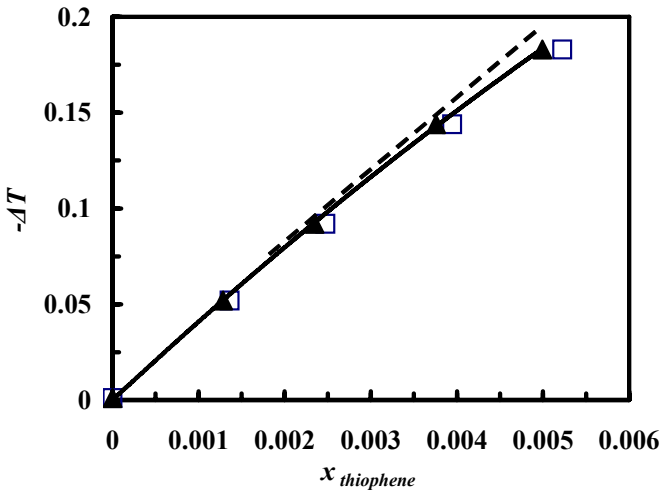

Figure 30 -*ΔT* as a function of feed composition for the system thiophene (1) in toluene (2) at 379.53 K; □, experimental values, ▲, equilibrium liquid composition, —, polynomial fitting, ---, limiting slope.

To test the reliability and accuracy of the system, the infinite dilution activity coefficients of ethanol (1) + water (2) were measured in the range from 333.15 K to 373.15 K. The results were compared with the literature data [60]. It can be seen that the agreement with the literature data is good, as shown in Figure 31.

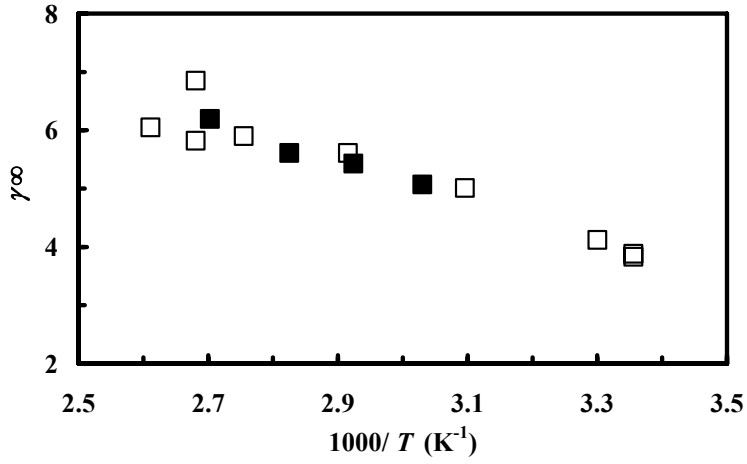

Figure 31 Comparison of experimental data to the literature for the infinite dilution activity coefficient of ethanol (1) in water (2): ■, this work; □, Kojima [60].

The results for the infinite dilution activity coefficients of 1-propanethiol, ethyl methyl sulphide, and thiophene in toluene, *n*-heptane, and 2,2,4-trimethylpentane at 90 kPa are presented in Table 9. The infinite dilution activity coefficients determined are compared with the predictive original UNIFAC group contribution model.

Table 9. Experimental values of γ^{∞} determined in this work together with 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-trimethylpentane	368.11	1.46	1.47
1-propanethiol	toluene	379.53	0.86	1.29
	n-heptane	367.47	1.04	1.31
	2,2,4-trimethylpentane	368.11	1.23	1.25
ethyl methyl sulphide	toluene	379.53	0.88	–
	n-heptane	367.47	1.18	1.20
	2,2,4-trimethylpentane	368.11	1.17	1.14

(–) not available

The experimental results show good agreement with the original UNIFAC prediction. The interaction parameter for the CH_2S – ACH-CH_2 binary pair is not available, and hence no UNIFAC prediction for the ethyl methyl sulphide + toluene system is possible.

The γ^{∞} values of sulphur compounds for the thiophene + toluene and thiophene + 2,2,4-trimethylpentane systems obtained from the recirculation still measurements are compared with the γ^{∞} values obtained from the comparative ebulliometer measurements. The agreement between measurements is good, as shown in Figure 32.

However, the γ^{∞} values of sulphur compounds for the 1-propanethiol + toluene and ethyl methyl sulphide + toluene systems obtained from comparative ebulliometer measurements are less than one. These systems show negative deviation from Raoult's law, and thus these systems do not follow the typical behaviour of sulphur compounds in hydrocarbons. The reason for this behaviour is the high relative volatility and the large differences in boiling point temperatures between the solutes and solvent. The temperature fluctuations during the measurements caused considerable deviation in the limiting slope calculation, and thus these γ^{∞} values are not reliable.

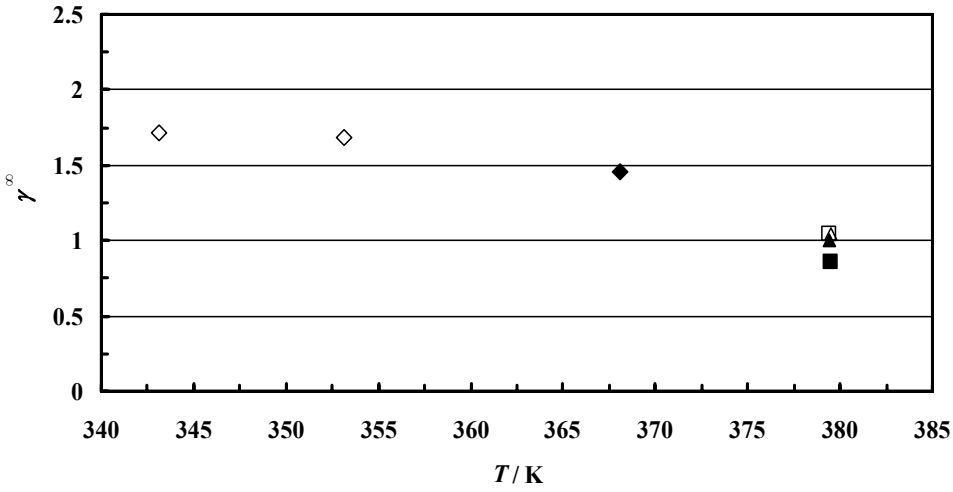

Figure 32 Comparison γ^{∞} obtained from extrapolated VLE measurements and direct comparative ebulliometry method: ■, 1-propanethiol + toluene at 379.53 K (comparative ebulliometry); □, 1-propanethiol + toluene at 379.44 K (VLE); Δ, thiophene + toluene at 379.53 K (comparative ebulliometry); ▲, thiophene + toluene at 379.44 K (VLE); ♦, thiophene + 2,2,4-trimethylpentane at 368.11 K (comparative ebulliometry); ◊, thiophene + 2,2,4-trimethylpentane at 343.15 K and 353.15 K (VLE)

6 CONCLUSIONS

We have measured and studied the vapour-liquid equilibrium behavior of selected sulphur compounds (1-propanethiol, diethyl sulphide, ethyl methyl sulphide, and thiophene) with various hydrocarbons under isobaric and isothermal conditions using a circulation still and comparative ebulliometer techniques.

The gamma (γ)–phi (ϕ) approach was used in the calculation of vapour-liquid equilibria. The activity coefficients of the liquid phase (γ) were correlated with the Wilson model. The Wilson model gave good correlation for all the systems. The activity coefficients at infinite dilution (γ^{∞}) were extrapolated from VLE measurements with the Wilson model. The temperature-dependent parameters of the Wilson model can be obtained by simultaneously using VLE measurements and excess enthalpy (H^{E}) measurements from the literature. This procedure normally leads to models that are applicable across a wide temperature range.

The measured VLEs were compared with the predicted VLEs from the original UNIFAC, UNIFAC-Dortmund, and COSMO-RS predictive models. The original UNIFAC is adequate to describe the behaviour of sulphur in hydrocarbons, even though its application is limited to the availability of the functional group interaction parameters. New measurements in this work will be used to determine the missing UNIFAC interaction parameters. When the measurements are not available, the original UNIFAC and COSMO-RS predictive models can be used to predict the activity coefficients. However, COSMO-RS gives poor prediction for all the systems studied, and thus currently it is not a suitable model for predicting the behaviour of systems containing sulphur compounds. All the VLE measurements passed the integral, infinite dilution, and point tests.

The γ^{∞} of sulphur compounds values for the thiophene + toluene and thiophene + 2,2,4-trimethylpentane systems obtained from the recirculation still measurements are compared with the γS^{∞} values of sulphur compounds obtained from the comparative ebulliometer measurements. The agreement between the measurements is reasonably good.

All the measured γ^{∞} of sulphur compounds in hydrocarbons are less than two. 1-Propanethiol, thiophene, and diethyl sulphide in toluene systems show ideal behaviour, thus the γ^{∞} of sulphur compounds for these systems are one. The activity coefficients of sulphur compounds in hydrocarbons show the typical behaviour of positive deviations from Raoult's law, which become smaller with increasing temperature and with an increase in alkane chain length.

However, the γ^{∞} of sulphur compounds for the 1-propanethiol + toluene and ethyl methyl sulphide + toluene systems obtained from the comparative ebulliometer measurements are less than one. These systems show negative deviation from Raoult's law, and thus these systems do not follow the typical behaviour of sulphur compounds in hydrocarbons. The reason for this behaviour is the high relative volatility and the large differences in boiling point temperatures between the solutes and solvent ($|\Delta T_b| \approx 40^0$ C). The temperature fluctuations during the measurements caused a significant deviation in the limiting slope calculation, and thus these γ^{∞} are not reliable. The experimental setup is not suitable for measuring these systems.

The systems 1-propanethiol, thiophene, and diethyl sulphide in toluene show nearly ideal behaviour. No azeotrope formation was observed for the systems thiophene + 1-hexene and

diethyl sulphide + 1-hexene. The reaction between 1-propanethiol and 1-hexene was observed. The circulation still cannot make measurements for reactive systems, and thus the measurements should be made with a special device for reacting systems.

The systems thiophene + *n*-hexane and thiophene + 2,2,4-trimethylpentane, as well as the systems diethyl sulphide + *n*-heptane and diethyl sulphide + 2,2,4-trimethylpentane, show positive deviations from Raoult's law. These systems exhibit maximum pressure azeotropy.

The systems thiophene + 1-hexene and thiophene + 2-ethoxy-2-methylpropane, as well as the systems of diethyl sulphide with *n*-hexane, 1-hexene, cyclohexane, and 2-ethoxy-2-methylpropane, show positive deviation and strong nonideality. No azeotropes formed in those systems.

The Bancroft point could be used as an indication of the formation of an azeotrope. A Bancroft point occurred at about 230 K for the 2-propanol + 1,1-diethoxyethane system when each vapour pressure was extrapolated to a lower temperature by the Antoine parameters. Azeotropic behaviour with a minimum boiling temperature was observed at T = 353.15 K, P = 94.2 kPa, x_1= 0.916 ± 0.005.

New measurements in this work gave new information about the behaviour of sulphur in hydrocarbons. However, more new experimental measurements for various systems containing higher molecule of sulphide, higher molecule of thiol, and alkylated thiophene in different hydrocarbons, together with excess enthalpy measurements, are needed for the design of multicomponent separation processes such as distillation columns.

The circulation still and ebulliometer are good techniques and are commonly used for vapour-liquid equilibrium determination in the low-pressure range. Other techniques can also be considered, such as a high-pressure ebulliometer and static cell apparatus to measure systems at high temperatures. Compared to a recirculation still, gamma infinite dilution measurements with comparative ebulliometers are more difficult to perform. When the relative volatility between the two components is large, pressure and temperature fluctuations are typically observed, which lead to inaccurate measurements. In addition, no thermodynamic consistency tests are available to check the γ^{∞} values.

REFERENCES

1. Satterfield, C.N. *Heterogeneous Catalysis in Industrial Practice*, 2nd Edition, McGrawHill, New York, 1991.
2. http://nesteoil.com/default.asp?path=1,41,538,2035,5196,5197,5199.
3. Twu, C. H., Tassone, V., Sim, W. D. Accurately predict the VLE of thiol-hydrocarbon mixture. *Chem. Eng. Prog.* **2004**, *100* (9), 39–45.
4. Knudsen, K. G., Cooper, B.H., Topsoe, H. Catalyst and process technologies for ultra-low sulfur diesel fuel. *Applied Catalysis*, *A: General* **1999,** *189*, 205-215.
5. Song, C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel, and jet fuel. *Catalysis Today* **2003,** *86*, 211-263.
6. Mochida, I., Choi, K.H. An overview of hydrodesulfurization and hydrodenitrogenation. *Journal of the Japan Petroleum Institute* **2004**, *47*, 145-163.
7. Gmehling, J., Onken, U. *Vapor-liquid equilibrium data collection*, DECHEMA Chemistry Data Series, Vol. 1, Part 6a; DECHEMA: Frankfurt/Main, 1980.
8. Gmehling, J., Onken, U. *Vapor-liquid equilibrium data collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 6b; DECHEMA: Frankfurt/Main, 1980.
9. Gmehling, J., Onken, U. *Vapor-liquid equilibrium data collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 7; DECHEMA: Frankfurt/Main, 1980.
10. Gmehling, J., Onken, U. *Vapor-liquid equilibrium data collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 8; DECHEMA: Frankfurt/Main, 1984.
11. Valtz, A., Schwartzentruber, J., Richon, D., Renon, H. Vapor liquid equilibria for volatile-sulfur-containing systems, *Gas Processor Association*, February **1994**.
12. Valtz, A., Guilbot, P., Richon, D. Vapor-liquid equilibria for volatile-sulfur-containing systems III. butane-sulfur compounds containing systems IV. hydrocarbon-hydrocarbon-sulfur compounds containing systems V. hydrocarbon(s) - hydrogen sulfide-sulfur compounds containing systems. *Gas Processor Association*, September **1998**.
13. Giles, N. F., Wilson, G. M. Phase equilibria on four binary systems: 1,2-dichloroethane + *trans*-1,2-dichloroethylene, 1-octene + 2-methyl thiophene, 2-ethyl thiophene + 2,2,4-trimethylpentane, and cyclopropanecarbonitrile + water. *J. Chem. Eng. Data* **2006**, *51*, 1973-1981.
14. Giles, N. F., Wilson, G. M. Phase equilibria on seven binary mixtures *J. Chem. Eng. Data* **2000**, *45*, 146-153.
15. Gmehling, J. *Activity Coefficients at Infinite Dilution*; DECHEMA Chemistry Data Series, DECHEMA: Frankfurt/Main, 1994.
16. Gmehling, J. *Heats of Mixing Data Collection*; DECHEMA Chemistry Data Series, Vol. 3, Part 1; DECHEMA: Frankfurt/Main, 1984.
17. Gmehling, J. *Heats of Mixing Data Collection*; DECHEMA Chemistry Data Series, Vol. 3, Part 2; DECHEMA: Frankfurt/Main, 1984.
18. Didaoui-Nemouchi, S., Ait Kaci, A. Excess molar enthalpies of binary mixtures of thiophene and diethyl sulfide with n-alkanes. *J. Thermal Anal.* **2002**, *69*, 669-680.
19. Philippe R., Ferhat-Hamida, Z. *Int. Data Series, Sel. Data Mixtures Ser. A* **1977**, 116.
20. Marongiu, B., Marras, G., Pittau, B., Porcedda S. Thermodynamics of binary mixtures containing thiaalkanes. Excess enthalpies of thiaalkanes and polythiaalkanes + n-alkanes or cyclohexane *Fluid Phase Equilib*. **1994**, *97*, 127-146.
21. Gmehling, J., Menke, J., Krafczyk, J., Fischer, K. *Azeotropic Data*; Wiley, 2004.
22. Desty, D. H., Fidler, F. A. Azeotrope formation between sulfur compounds and hydrocarbons. *Ind. Eng. Chem.* **1951**, *43*, 905-910.

23. Lecat, M. Azeotropes of sulfides and halides. *Bull. Classe Sci. Acad. Roy. Belg*. **1947**, *33*, 160-182.
24. Denyer, R. L., Fidler, F. A., Lowry, R. A. Azeotrope formation between thiols and hydrocarbons. *Ind. Eng. Chem*. **1949**, *41*, 2727-37.
25. Woody, L., Marshall, H. *Sulfur distribution prediction with commercial simulators*. Proceedings of the Laurance Reid Gas Conditioning Conference **1996**, 254-282.
26. Lindberg, T., *Calculation of Sulfur Compounds in Simulations*, Master thesis, Lappeenranta University of Technology, 2003. (in Finnish)
27. Fredenslund, A., Gmehling, J., Rasmussen, P. *Vapor–Liquid Equilibria Using UNIFAC − A Group Contribution Method*; Elsevier: Amsterdam, 1977.
28. 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.
29. 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.
30. Wittig, R., Lohmann, J., Gmehling, J. Prediction of phase equilibria and excess properties for systems with sulfones. *AIChE J*. **2003**, *49*, 530-537.
31. Yerazunis, S., Plowright, J.D., Smola, F.M. Vapor-liquid equilibrium determination by a new apparatus. *AIChE J.* **1964**, *10*, 660-665.
32. Aittamaa, J., Pokki, J.-P. *User manual of program VLEFIT*; Helsinki University of Technology: Espoo, 2003.
33. Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197-1203.
34. Eckert, F., Klamt, A. Fast solvent screening via quantum chemistry: COSMO-RS approach. *AlChE J*. **2002**, *48*, 369-385.
35. Swietoslawski, W. *Ebulliometric measurements*, New York: Reinhold, 1945.
36. Eckert, C. A., Newman, B.A., Nicolaides, G.L., Long, T.C. Measurement and application of limiting activity coefficients. *AIChE J*., **1981**, 27, 33.
37. Prausnitz, J. M., Lichtenthaler, R. N., de Azevedo, E. G., *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd Edition, Prentice-Hall, Englewood Cliffs, 1986.
38. Smith, J. M., van Ness, H. C., *Introduction to Chemical Engineering Thermodynamics*, 4th Edition, McGraw-Hill, New York, 1987.
39. Reid, R. C., Prausnitz, J. M., Poling, B. E., *The Properties of Gases and Liquids*, 4th Edition, McGraw-Hill, New York, 1987.
40. Peng, D. Y., Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem.: Fundamentals*. **1976**, *15*, 59-64.
41. Yaws, C. L., *Chemical Properties Handbook*, McGraw-Hill, New York, 1999.
42. Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514-517.
43. 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.
44. Renon, H., Prausnitz, J.M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J*, **1968**, *14*, 135-144.
45. Abrams, D. S., Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess gibbs energy of partly or completely miscible system, *AIChE J*. **1975**, *21*, 116-128.
46. Pokki, J.-P. Development of Vapour Liquid Equilibrium Calculation Methods for Chemical Engineering Design, Dissertation, Helsinki University of Technology, 2004, 24-28.

47. Gautreux, M. F., Coates, J. Activity coefficients at infinite dilution, *AIChE J*. **1955**, *1*, 496-500.
48. Dohnal, V., Novotná, M. Infinite-dilution activity coefficients by comparative ebulliometry: A model of ebulliometer and the experimental equipment and procedure, *Collect. Czech. Chem. Commun*. **1986**, *51*, 1393-1402.
49. Tsonopoulos, C. Empirical correlation of second virial coefficients. *AIChE J*. **1974**, *20*, 263-272.
50. Raal, J. D. Characterization of differential ebulliometers for measuring activity coefficients. *AIChE J*. **2000**, *46*, 210-220.
51. Klamt, A., Schüürmann, G. COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans. 2* **1993**, *5*, 799-805.
52. Klamt, A. Conductor-like Screening Model for Real Solvents: A new approach to the quantitative calculation of solvation phenomena. *J. Phys. Chem.* **1995,** *99*, 2224-2235.
53. Klamt, A. *COSMO-RS from Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*; Elsevier, 2005.
54. 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.
55. Eckert, F., Klamt, A. *COSMOtherm*, Version C2.1, Release 01.05; COSMOlogic GmbH &Co. KG: Leverkusen, Germany, 2005.
56. Pennington, R.E.; Scott, D.W.; Finke, H.L.; McCullough, J.P.; Messerly, J.F.; Hossenlopp, I.A.; Waddington, G. The chemical thermodynamic properties and rotational tautomerism of 1-propanethiol. J. Am. Chem. Soc. 1956, 78, 3266-3272.
57. 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.
58. Gmehling, J., Onken, U. *Vapor–Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol. 1, Part 1; DECHEMA: Frankfurt/Main, 1977.
59. Kojima, K., Moon, H., Ochi, K. Thermodynamic consistency test of vapor-liquid equilibrium data. *Fluid Phase Equilib*. **1990**, *56*, 269-284.
60. Kojima, K., Suojiang Z., Hiaki, T**.** Measuring methods of infinite dilution activity coefficients and a database for systems including water. *Fluid Phase Equilib* **1997**, *131*, 145-179.

APPENDIX I

Current matrix of phase equilibria measurements for organic sulphur compounds and hydrocarbons