

Viscosity and Density of Asymmetric Hydrocarbon Mixtures

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A thesis submitted for the degree of Doctor of Philosophy

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August, 2016

Declaration of Originality

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I hereby certify that all material in this thesis which is not my own work, has been properly acknowledged.

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Dedication

Dedicated to my parents

Acknowledgements

Acknowledgements

Firstly, I would like to express my profound gratitude to my supervisor Prof. J.P Martin Trusler for his enormous contributions, patience and support towards the success of this work. Indeed, this thesis would not have been possible without your constant and tireless advice and professional guidance. In addition to the invaluable technical skills I have learnt from you during this journey, your wealth of experience and critical approach to solving problem have sharpen my skills and reasoning ability in tackling challenges in life. My special gratitude goes to Prof. Velisa Vesovic and his group, for greatly assisting with some of the modelling approaches. In particular, my appreciation goes to Dr. Binh Nguyen and Dr. Nicolas Riesco for helping with the VW calculations. Although, not any longer with us at Imperial, I am very grateful to my academic mentor Dr. Edo Boek for his words of encouragement and guidance at the initial stage of this journey.

I also owe a great deal of thanks to all our colleagues in both thermophysical properties and the QCCSRC groups. Indeed the regular Thursday group meetings and the Friday QCCSRC seminars, have broaden my knowledge of various aspects of thermophysical property measurements, and the pleasant interaction with everyone in both groups is greatly acknowledged especially; Prof. Geoffrey Maitland, Dr. John Crawshaw, Dr. Ian Macdonald, Dr. Saif Al Ghafri, Dr. Mihaela Stever, Dr. Yolanda Vicente, Dr. Inês Graca, Dr, Chidi Efika, Dr. Geraldine Torin, Florence Chow, Rayane Hoballah, Julian Tay, Bian Hao, Claudio Calabrese, Benaiah Anabaraonye, Lorena dos-Santos, Sultan Al-Habsi and Theodor Videnberg, indeed, I have enjoyed my stay in your midst and from each of you, I have learnt a lot and, I sincerely thank you for that. I would also like to specially thank the people from the mechanical and electrical workshops, in particular: Gavin Barnes, Richard, Chin Lang and Arafat for their impressive craftsmanship and display of raw talents in attending to our unending problems. Really, you all played an invisible role towards achieving this project.

I am highly indebted to my parents Alhaji Muhammad Alkali Ibrahim and Late Malama A'ishatu Muhammad for their parental care, love and support within and outside my academic pursuits. Really, no word can express my appreciations to you for all the role you both played in making me who I'm today, I can only pray that may Allaah (SWT) in his infinite mercy rewards you with Aljannatul Firdaus. Similarly, I'm deeply grateful to the members of my family who stood by me at all times and for their moral and spiritual support especially Alhaji Mohammed Nakaduna, Baba Alkali, Ibrahim Alkali and the entire members of Sarkin Fada's family. To them, I'm very grateful.

Acknowledgements

I would like to specially thank my dear wife Dr Zainab Muahmmad Abba and my little daughter Aisha Humayra for their love, patience, prayers and understanding during this journey. They have been very supportive and stood by me during a long hard time while I was completing this thesis. I really appreciate them and I wish I can do more than just writing a few words.

I wish to express my appreciations to the Federal Government of Nigeria for offering me a postgraduate scholarship under the “2010 NYSC President’s Honours Award scheme”. My sincere gratitude goes to the management and staff of Petroleum Technology Development Funds (PTDF) for their prompt and regular payment of all expenses towards this project including my monthly up-keep allowances.

Finally, I say a big THANK you to everyone that contributed in one way or the other in achieving this success.

Malami Mohammed, 2016

Abstract

The main focus of this research has been on providing useful experimental viscosity and density data on some representative asymmetric hydrocarbon mixtures with particular interest on mixtures of higher-molecular-weight aliphatic hydrocarbons with dissolved methane.

This thesis details incremental improvements in the design and operation of an existing vibrating-wire viscometer-densimeter (VWVD). These improvements were necessary in order to allow safe investigations of viscosity of highly flammable mixtures such as methane + *n*-hexadecane. The procedure for absolute viscosity measurement using the VWVD is described in detail. In the absolute mode of operation, the properties of the vibrating-wire (i.e. radius and length) and that of the suspended sinker (i.e. mass and volume) were determined via independent mechanical measurements. The diameter (and hence the radius) of a centreless-ground tungsten wire was measured accurately using a laser micrometer whereas the length of the wire was carefully measured with an internal caliper. The mass and volume of the suspended sinker were determined via hydrodynamic weighing methods.

Simultaneous viscosity and density measurements were made on binary mixtures of *n*-hexadecane, 2,6,10,15,19,23-hexamethyltetracosane (Squalane) or cyclohexane with dissolved methane each at four different compositions. Measurements were made in the temperature range from (298.15 to 473.15) K, pressure range (0.1 to 200) MPa and methane mole fractions x_1 (0 to 0.4) with an overall combined expanded uncertainties within 0.3 % in density and 2 % in viscosity with a coverage factor $k = 2$. Additional measurements were conducted on perfluoropolyether (also known as krytox® GPL 102) over the same temperature and pressure range. The data generated were successfully correlated for density using the modified Tait equation and for viscosity, by means of the Tait-Andrade equation. These correlations described most of the data to within their expected uncertainties.

In an attempt to model the viscosity of the binary mixtures, the extended hard sphere model was tested both in predictive and correlative approaches using different mixing rules. Surprisingly, in the predictive mode, the results indicated that, the conventional linear mole-fraction average rule provided a better prediction with a maximum absolute deviations ($\Delta_{MAD,\eta S}$) in viscosity ranging from (9 to 64)% compared to the quadratic and the other more complicated combining rules such as the Van der Waals rules. This was observed

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consistently across all the three binary systems investigated in this work. In the correlative mode however, the maximum absolute deviations were in the range from (3 to 33) % when the molar core volumes of each mixture composition were treated as adjustable parameters with the higher $\Delta_{MAD,\eta}$ s mostly observed in the mixtures of methane + squalane. Furthermore, the performance of the extended hard sphere scheme and the Vesovic-Wakeham (VW) model in predicting the viscosity of asymmetric mixtures were tested. This was done by comparing the predicted results from both models against the experimental data obtained in this work. In this regard, three performance indicators namely: the maximum absolute deviations ($\Delta_{MAD,\eta}$); the average absolute deviations ($\Delta_{AAD,\eta}$) and the average bias ($\Delta_{bias,\eta}$) of these models were compared. It was found that the VW model consistently produced lower values of all these quantities for the two binary systems investigated. For example, for the mixture of methane + *n*-hexadecane the $\Delta_{MAD,\eta}$ s obtained from the VW model range from (10 to 31)%, whereas those of the extended hard sphere model range from (10 to 47)%. On the basis of our analysis, the VW model seems to be more promising and therefore more likely to be recommended for predicting the viscosity of asymmetric mixtures.

Finally, the results obtained from this project extend our knowledge and basic understanding of the viscosity characteristics of the so-called asymmetric mixtures especially to higher temperatures and pressures.

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Nomenclature

Nomenclature

Definitions of commonly used symbols are given below:

a	End correction factor of vibrating wire
A	Amplitude
B_n	Second virial coefficient
B	Magnetic field strength
d	Damping parameter; Diameter
D	Diffusion coefficient
E	Young's modulus
f	Frequency
f_0	Resonance frequency in vacuum
f_b	Bandwidth
F	Force; Flow rate
g	Gravitation acceleration
h	height
I_a	Second moment of inertia
J	Bessel function
k	Radius of gyration; Boltzmann's constant
K	Modified Bessel function
L	Length
m	Mass; Kinetic energy correction factor; Molecular mass
M	Bending moment; Torque
M_a	Match number
N_A	Avogadro number
n	End correction factor; number of moles
p	Pressure
Q	Volumetric flow rate; Resonance quality factor; Heat
R, r	Radius; Universal gas constant
S	Cross section
s	Laplace conjugate to r ; Specific entropy
t	Time
T	Period; Tension; Temperature
u, v	Velocity; Speed
V	Voltage; Volume

Nomenclature

V_1	Induced emf from motion of vibrating wire
V_2	Voltage due to electrical impedance of stationary wire
V_m	Molar volume
V_0	Characteristic core volume for closed packed spheres
w	Mass fraction
W	Work
x	Mole fraction
X	Generic transport property
x,y,z	Rectangular coordinates
Z	Compressibility factor

Greek symbols:

α	Angular displacement
β	Dimensionless added mass
β'	Dimensionless viscous damping
γ	Rate of strain; adjustable parameter
δ	Scaling parameter
Δ	Logarithmic vacuum decrement
ε	Intermolecular energy potential
η	Dynamic viscosity
θ	Dimensionless period; Scaling parameter
κ	Geometric constant; End correction parameter of the wire
λ	Thermal conductivity
Λ	Amplitude
μ	Wave number
ν	Kinematic viscosity
ρ	Density
σ	Rigid sphere diameter; Shear stress
τ	Shear rate; Dimensionless time
φ	Wire curvature
χ	Pseudo-radial distribution function; Shape factor
ω	Angular frequency
Ω	Collision integral
ψ	Stream function
Z	Dimensionless displacement

Nomenclature

Subscripts:

0	First resonance; <i>In vacuo</i>
Al	Aluminium
b	Bandwidth
c	Critical; Container
cal.	Calculated
E	Enskog
exp	Experimental
max	Maximum
r	Resonance
s	sinker
w	wire
W	Tungsten
YS	Yield stress
vac	<i>In vacuo</i>
x,y,z	Rectangular co-ordinate planes
r,θ,z	Polar co-ordinate planes

Introduction

1.1 Background to the research

The viscosity is a key transport property that influences the flow of fluids. It is an important property in many engineering research and applications; ranging from the design of process equipment to the simulation of production profiles of oil wells and reservoirs. In the area of research, knowledge of viscosity data helps in pressure drop calculations, heat and mass transfer determinations etc. For industrial applications on the other hand, accurate knowledge of viscosity is important in many oil and gas processes. For instance, in oil exploration, the selection of a production technique as well as the design of processing facilities largely depends on the viscosity of the crude oil in the reservoir in question. In addition, accurate knowledge of viscosity is particularly important in some specific oil and gas processes. These processes include heavy oil viscosity upgrade, production and transportation, carbon capture and storage (CCS) and enhanced oil recovery (EOR). The importance of accurate viscosity data cannot be overemphasized especially in the oil and gas industry. This is because inaccurate viscosity data could lead to significant loss of revenue to the oil companies. To illustrate this, recent studies[1] have showed that an error of 1% in viscosity data could translate to a deviation of up to 7% in cumulative oil production.

The quest for more energy resources as a result of increasing global human population and continuous depletion of the conventional crude oil resources; coupled with the scientific and technological advancement in the area of petroleum exploration and production, have led to increasing research activities in the areas of maximizing the recovery of conventional resources and also a tremendous increase in the exploitation of the unconventional resources such as heavy and extra-heavy oil. In the area of improving the recovery of conventional petroleum resources, it is widely known that the primary recovery method in which the reservoir pressure is the main driving force only recover up to 30 % of the original oil in place (OOIP). The secondary recovery method via water injection helps to boost the recovery into the range of (30 to 60) % of the OOIP. The tertiary recovery method also known as enhanced oil recovery assists in additional recovery of up to 80 % of the OOIP. The enhanced recovery via the injection of carbon dioxide, CO₂-EOR[2-6], has been widely employed by the oil industry due to its dual advantages of improved recovery and simultaneous carbon storage. In this technique, CO₂ is injected into an underground depleted reservoirs in order to increase sweep efficiency and solubilize the residual hydrocarbons to aid the recovery of the remaining oil. This however, leads to the formation of asymmetric mixtures as most of the remaining

reservoir fluids consist of predominantly higher-molecular weight hydrocarbons.

In the area of exploiting unconventional crude oil resources, heavy oil is an unconventional energy source with high viscosity and relatively low API gravity index (defined in equation 1.0) typically < 22.3°[7] as shown in Figure 1.0.

$$\text{API Gravity} = \left[\left(\frac{141.50}{\gamma} \right) - 131.50 \right] \quad (1.0)$$

where, γ is the relative density at $T = 288.15 \text{ K}$

This type of oil have been recognised as the most abundant unconventional energy resource capable of replacing the rapidly declining reserves of light and medium oil. For instance, estimates[8-11] have shown that heavy oil together with extra heavy oil and natural bitumen constitute about 70 % of the world's total recoverable oil resources discovered to date as shown in Figure 1.1.

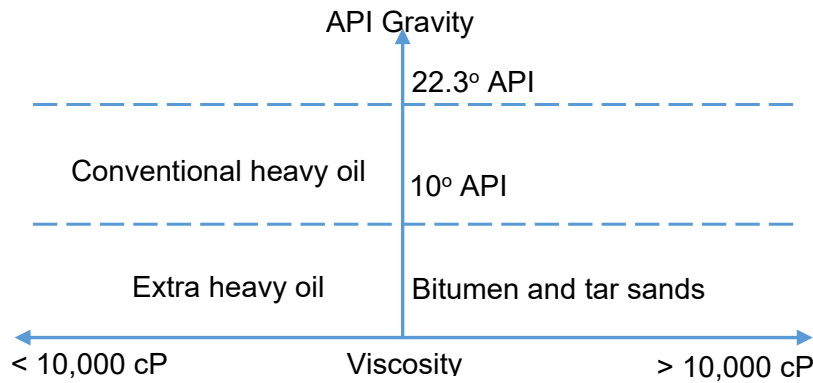


Figure 1.0: Classification of heavy and extra-heavy oil based API gravity and viscosity[7]

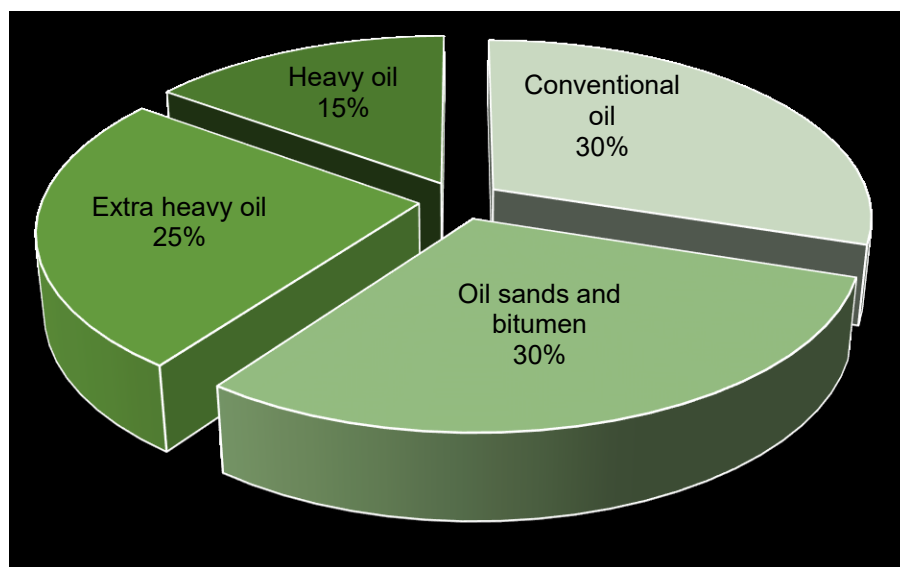


Figure 1.1: Estimation of total world's oil reserves[11]

However, extraction of heavy and extra heavy oil often necessitate viscosity reduction of

the original crudes in order to meet certain requirements for processing and transportation. There are several techniques for viscosity upgrade employed by the oil industries notable ones includes: addition of water; addition of steam; and addition of diluents. Addition of water entails re-injecting the produced water back in to the reservoir in order to reduce the viscosity and improve recovery of the heavy crude. This however often leads to the formation of water-in-oil emulsions whose viscosity could be several order of magnitudes higher than the original heavy crude.

Addition of steam can be done in so many ways which include^[12]: the cyclic steam stimulation[13] (CSS), steam assisted gravity drainage[14] (SAGD) etc. In the CSS process also known as 'huff and puff', steam is injected in to the formation through an injection well and allowed to heat up the reservoir for a specified period of time known as 'soak period', the production well is then opened to recover the heated oil and steam condensate. When the production rate decline, the cycle is then repeated until the oil in the formation is drained. The SAGD process on the other hand involves drilling of pair of coextensive injection and production wells near the base of the formation. The wells are drilled one above the other and typically spaced within 5 – 8 meters. Steam is injected though the wells at a pressure lower than the fracturing pressure of the formation. The oil absorbed the heat and become mobile and eventually drained downwardly in to the lower well as its viscosity is reduced. The lower well is then opened to produce the heated oil and some steam condensate[12]. Addition of steam is however associated with high cost of heating and therefore energy intensive.

Addition of low-molecular weight hydrocarbons to serve as diluents usually provides a convenient way of reducing the viscosity of heavy oil. In this approach, light miscible components (such as CH₄, C₂H₆ C₃H₈ etc.) are added to the heavy crude to reduce its viscosity which eventually leads to the formation of asymmetric mixtures.

On the other hand, providing sufficient energy to meet the growing energy demand while avoiding the dangerous climate change has been identified as the greatest challenge for the oil industry in this century. The storage of CO₂ in deep geological formations via carbon capture and storage (CCS) has been widely considered as an initial step for tackling greenhouse gas emissions and mitigating climate change[15-19]. In CCS, just as in CO₂-EOR, the CO₂ is captured and injected into an underground reservoirs for permanent storage. However, during the storage process CO₂ eventually get mixed with the hydrocarbons and other reservoir fluids to form asymmetric mixtures.

An asymmetric mixture is defined as a mixture in which there are considerable differences in size, shape, flexibility or energetic interactions in the molecules of the mixture[20].

Asymmetric mixtures of hydrocarbons with light gases (CH_4 , CO_2 etc) have become an interesting area of scientific research in the past few decades due to their wide existence in many oil and gas processes such as EOR and CCS. Consequently, reliable thermophysical property data such as density and viscosity of these important fluids are required for effective design and simulation of these oil and gas processes. For example, in both CO_2 -EOR and CCS processes, knowledge of viscosity of CO_2 + hydrocarbons mixtures permits the characterization of the flow pattern of the fluid in the subsurface and also, helps to identify regions for optimum penetration of the CO_2 in both processes. On the other hand, knowledge of the density of this fluid mixture helps in determining the time required for effective containment of CO_2 underground during CCS process. In addition, accurate and reliable viscosity data of asymmetric mixture are required to design transport equipment and also to simulate production profiles of petroleum reservoirs of heavy oil.

1.2 Problem statement and motivations

Viscosity data of highly asymmetric systems containing high molecular weight liquids and gases are very important for the design of certain industrial processes. Such data are however very limited in the literature due to the expensive and time-consuming nature of running laboratory experiments on these complex mixtures. Consequently, there are gaps in the viscosity data of highly asymmetric mixtures in the literature and this, lead to poor understanding of the theory of the viscosity of these important fluids. A literature survey reveals that most of the previous viscosity studies on this type of fluid involved semi-asymmetric systems (i.e. mixtures of light gases with medium-molecular-weight hydrocarbons), which might not be the ideal representative of crude oil, especially heavy oil. For instance, while binary mixtures of methane + *n*-decane have been studied extensively in the past, there are virtually no data published to the author's knowledge on the viscosity of mixtures of either methane + *n*-alkanes or CO_2 + *n*-alkanes with carbon number, $C > 18$. Table 1.1 presents a results of a search of available literature data on the viscosity of mixtures of methane + *n*-alkanes and CO_2 + *n*-alkanes. It was also observed that there was no published data on the viscosity of either C_1 or CO_2 in a mixture with C_{15} , C_{16} , or C_{17} in the literature as can be seen in Table 1.1. Consequently, the present work seek to fill some existing gaps in the literature by providing reliable data on the viscosity and density of binary mixtures of higher-molecular weight hydrocarbons with dissolved methane.

It is important to note that no mixture involving CO_2 was measured in this work as the present work is a continuation of the previous study by Ciotta *et al.*[21-23] in which some CO_2 + hydrocarbon systems were measured.

Table 1.1: Literature data on the viscosity of methane (1) + *n*-alkanes (2) and CO₂ (1) + *n*-alkanes (2) mixtures

<i>n</i> -alkane	Viscosity of CH ₄ (1) + <i>n</i> -alkane (2)			Viscosity of CO ₂ (1) + <i>n</i> -alkane (2)		
	<i>T</i> /K	<i>p</i> /MPa	Ref.(s)	<i>T</i> /K	<i>p</i> /MPa	Ref.(s)
Methane	-	-	-	293 to 473	0.1 to 2.5	[24-26]
Ethane	100 to 523	0.1 to 35	[27-29]	210 to 468	0.1 to 37	[30, 31]
Propane	123 to 524	0.1 to 61	[28, 29, 32, 33]	298 to 551	0.1	[28, 30, 34]
Butane	278 to 633	0.1 to 55	[24, 29, 35, 36]	298 to 468	0.1	[30]
Pentane	373	-	[37]	-	-	-
Hexane	256 to 373	0.6 to 8.2	[37, 38]	-	-	-
Heptane	185 to 373	1 to 11.8	[37, 39]	-	-	-
Octane	290 to 430	-	[37, 40]	-	-	-
Decane	276 to 431	0.6 to 140	[20, 38, 40-47]	311 to 403	1.1 to 35	[48-52]
Tetradecane	294 to 448	-	[53]	323 to 373	0.9 to 6.0	[50, 51]
Octadecane	323 to 448	10	[54]	323 to 373	0.9 to 5.9	[49, 55]

Furthermore, even where a laboratory experiment is inexpensive, it is not realistic to carry out measurements on all fluid and at every thermodynamic state of interest, and so developing theoretical model for predicting the viscosity of the representative group of fluid samples is necessary. For pure hydrocarbons, several models based on well-understood and well-developed theories are readily available in the literature. These models are relatively simple mathematical expressions that can be used to estimate the viscosity of such fluids with sufficient accuracy. For hydrocarbon mixtures, there are very few models and these are mostly based on the viscosities of the pure components of the mixture by taking advantage of certain mixing rules. However, the prediction accuracy of such models depends on the type and/or nature of the individual components in the mixture. For instance, for simple liquid mixtures where all the components are similar, simple mixing rules such as those of Grunberg-Nissan[56] methods provide satisfactory estimations of the mixture viscosity. For asymmetric mixtures on the other hand, those simple mixing rules failed to provide good estimations because of the differences in the nature and sizes of the constituent molecules in the mixtures.

Two theoretical models (the VW and HS models) were found to be promising in predicting the viscosity of asymmetric mixtures. However, these models were poorly tested on the mixtures of highly asymmetric systems, as measured data were scarce in the literature. These models performed creditably well in predicting the viscosity of a simple hydrocarbon liquid mixtures. For instance, for binary liquid mixtures of *n*-octane + *n*-dodecane studied by Caudwell[57] and *n*-hexane + *n*-hexadecane studied by Aucejo *et al.*[58], despite high molar mass ratios of the constituents of these mixtures, both models

predicted the viscosities of these mixtures with less than 3 % average absolute relative deviations $\Delta_{AARD,\eta}$ relative to the experimental data as will be seen in section 4.

Moreover, the predicted results from the two models were compared for highly asymmetric binary mixtures of CO_2 + *n*-hexadecane studied by Ciotta[22]. Here, the two constituents of the mixture differ greatly in size and also, the molar mass ratio between the components is far greater than unity. In this case we observed that the predictions from the two models differed significantly. While the VW model produced an $\Delta_{AARD,\eta}$ of about 6 %, the hard sphere model on the other hand presented as much as twice $\Delta_{AARD,\eta}$ of VW model. So apparently, there is a difference in terms of the potentials of the two models in predicting the viscosity of highly asymmetric mixtures, and unfortunately, very few experimental data exist in the literature to further explore this potentials. Therefore, more experimental data on highly asymmetric systems are required to further test the performances of these models. In this research, highly asymmetric mixtures of methane + *n*-hexadecane, methane + squalane and methane + cyclohexane will be studied and the results will be used to test the performances of the two aforementioned theoretical models.

1.3 Aims and objectives

The aims and objectives of this research can be broadly grouped under the following headings:

- i. Experimental measurements to provide reliable density and viscosity data
This involved simultaneous density and viscosity measurements on binary mixtures of representative heavy hydrocarbons with dissolved methane with a view to providing reliable experimental data to fill some gaps identified in the literature. The measurements would be made under extreme conditions of temperatures in the range (273 to 473) K and pressure up to 200 MPa using a vibrating-wire viscometer-densimeter (VWVD) operated in an absolute mode.
- ii. Correlation and modelling

Simple empirical expressions available in the literature will be used to correlate the experimental data collected in (i) with the view to estimate both properties (i.e. density and viscosity) at any given state point within the temperature and pressure range investigated. Similarly, when applied with caution, these correlations can also be used to extend the datasets to even outside the investigated region to obtain a qualitative idea on both quantities. The modified Tait equation was used

to correlate the density, whereas for viscosity, the Tait-Andrade equation was employed to provide useful correlations of the experimental results for both pure and mixtures investigated in this work.

On the modelling approach, the initial plan was to compare to the experimental viscosity results with the predictions from two promising theoretical models namely: the original hard sphere model of Dymond and Assael (DA); and the Vesovic-Wakeham (VW) model. However, the original hard sphere model was not employed in the final analysis due to some compatibility issues with some of the mixtures investigated in this work. Instead, an extended version of hard sphere model which gives an improved accuracy in the high density region is more suitable for these types of fluid mixtures and therefore, it was employed in the analysis. Nonetheless, a critical assessment of the performance of both DA and VW models in predicting the viscosity of some asymmetric mixtures was made in chapter 4. The analysis was made using some 1567 viscosity data points of different types of hydrocarbon mixtures with various degrees of asymmetry obtained from 12 independent studies. Furthermore, the VW model was also not implemented for binary mixtures involving squalane, due to the lack of suitable correlation to describe the viscosity of pure squalane in the model. More so, the extended hard sphere model was also used to model the viscosity of the binary mixtures by testing several mixing rules with the aim of identifying the most suitable combining rule for predicting the viscosity of asymmetric mixtures using this model.

1.4 Scope and limitations of the project

Although crude oil is a complex multi-components mixture of an uncountable number of compounds, including water, salt, acid gases and straight chain, branched and aromatic hydrocarbons, this project was limited to the experimental measurement of viscosity and density of mixtures of higher-molecular-weight hydrocarbons with dissolved methane. It is also worthy of note, that the research focused more on the mixtures of some representative aliphatic hydrocarbons rather than the aromatics components. This is because it is extremely difficult to correlate some functional groups using theoretical approach such as VW model. Furthermore, in view of the extreme difficulties of simultaneous viscosity and density measurements using the VWVD apparatus coupled with time constrain, the experimental part of the research was limited to study on three representative systems of asymmetric mixtures highlighted above.

On the modelling aspect, the project did not seek to develop a new model; however, a critical analysis of the performance of the two identified models will be made with the view to identifying the most suitable for application to the asymmetric mixtures. Also an attempt will be made to identify suitable mixing rule to be used with the extended hard-sphere model to predict the viscosity of asymmetric mixtures.

1.5 Structure of the research

The research has been broken down into a number of activities for simplicity, and was designed to adopt the following structure.

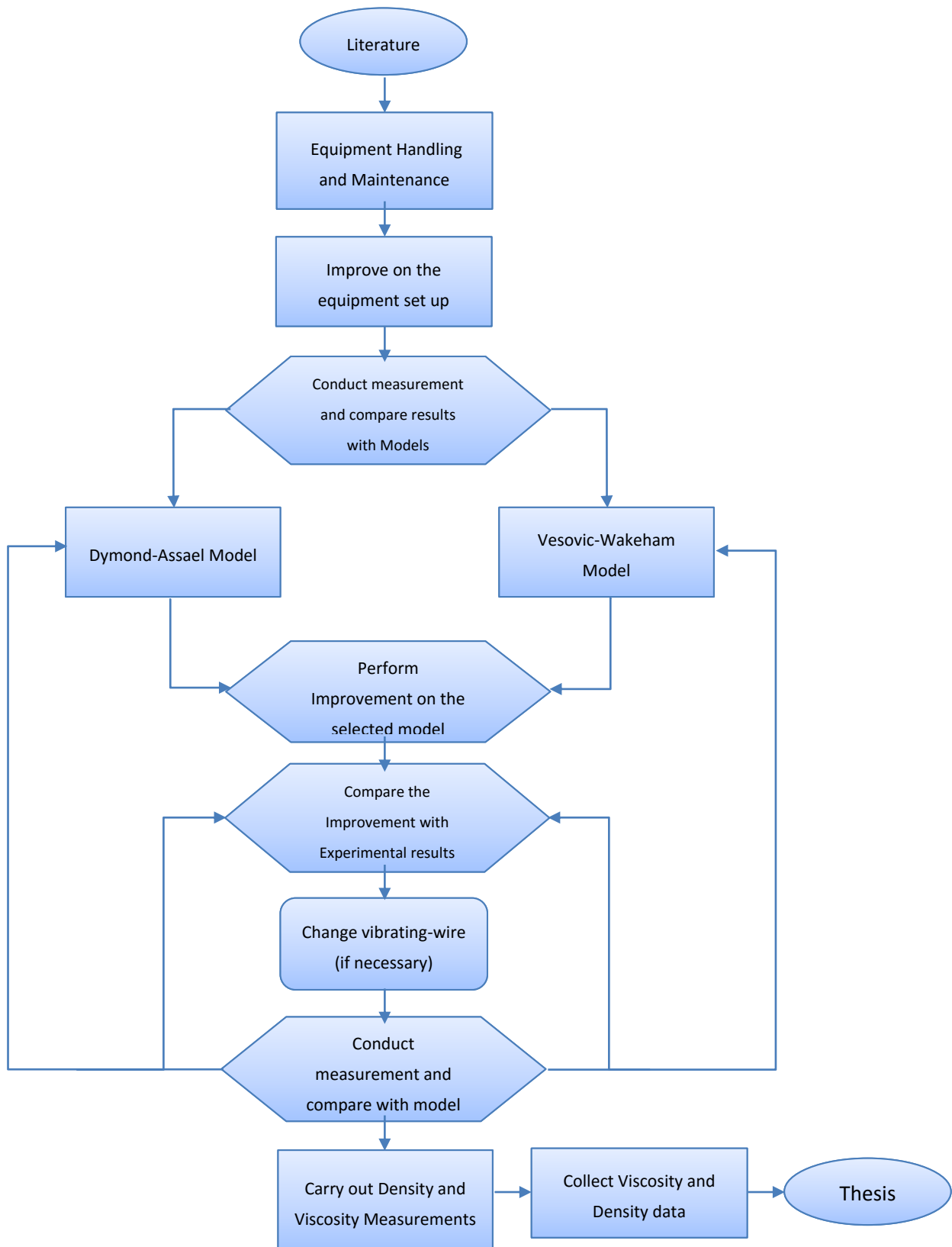


Figure 1.2: Structure of the research

1.6 Outline of the thesis

The outline of thesis is as follows:

- i. Chapter one gives a general introduction to the study, and presents an exhaustive analysis of the problems that necessitated carrying out the research. It also briefly highlighted the aims and objectives as well as the scope and imitations of the work.
- ii. Chapter two presents a review of various viscosity measurement techniques and also gives a comprehensive account of experimental viscosity data on asymmetric mixtures available in the literature
- iii. Chapter three highlights the theoretical background of vibrating-wire viscometer and a review of a number of studies conducted using vibrating-wire viscometer.
- iv. Chapter four highlights a general background to viscosity modelling and also presents a critical analysis on the performance of the original hard sphere model of Dymond-Assael and the Vesovic-Wakeham model in predicting the viscosity of various asymmetric systems.
- v. Chapter five presents the experimental methods along with a full description of the apparatus employed and also highlights some major incremental improvements in the design and the subsequent re-commissioning of the 2 kbar vibrating-wire viscometer.
- vi. Chapter six presents the operating procedure of the two types of vibrating-wire viscometers namely: vibrating-wire tensioned by a suspended sinker at the bottom; and a vibrating-wire clamped at both ends
- vii. Chapter seven present results, correlations, modelling and discussion of the data gathered in this project.
- viii. Chapter eight summarises the findings of this project and gives some conclusions and future works.

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Literature Review

2.1 Concept of viscosity

Fundamentally, viscosity is an intrinsic transport property of all fluids which can be defined as a degree of frictional resistance to flow or shear in a given medium. Viscosity is a state function of thermodynamic state variables, e.g. temperature, pressure and composition. Temperature and pressure affects the viscosity of both liquids and gasses, and the effect of temperature on viscosity is more pronounced in liquids than in gases.

In other words, dynamic viscosity can be defined as a tangential force per unit area required to slide one layer *A* against another layer *B* in the bulk of a moving fluid[1] as illustrated in Figure 2.1. In Figure 2.1, the force *F* causes the two layers *A* and *B* to slide at different velocities v_1 and v_2 .

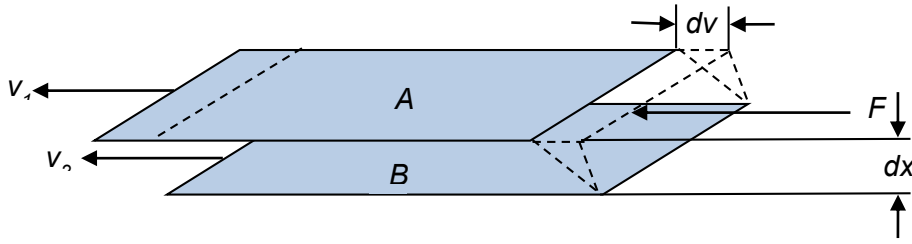


Figure 2.1 Shear of a liquid film in a moving fluid

The Newton's law of viscosity relates shear stress and the rate of strain of a moving fluid to viscosity as shown in the following expression.

$$\tau = -\eta \dot{\gamma} \quad (2.1)$$

where, τ is the shear stress, η is the proportionality coefficient and it is a property of the fluid, and $\dot{\gamma}$ is the rate of strain and it is a function of velocity and the distance between the plates as shown below:

$$\dot{\gamma} = \frac{1}{x} \frac{dx}{dt} = \frac{v}{x} \quad (2.2)$$

where, x is the distance between the plates and $\frac{dx}{dt}$ is the velocity of the plates; therefore

$$\eta = \tau \frac{x}{v} \quad (2.3)$$

For fluids that obeyed the Newton's law of viscosity (also known as Newtonian fluids), equation 2.1, the viscosity is independent of the shear stress and shear rate. Kinematic viscosity on the other hand is related to the density ρ , of the sample at same temperature and pressure conditions and it is defined by:

$$\nu = \frac{\eta}{\rho} \quad (2.4)$$

where, ν is the kinematic viscosity, η is the dynamic viscosity and ρ is the density

The viscosity can be obtained in two ways via primary or secondary sources. In this context, the primary source is by conducting laboratory measurement, while the secondary source is by estimating using appropriate predicting models. In the subsequent sections, a review of some laboratory techniques of obtaining viscosity will be given.

2.2 Review of viscosity measurement techniques

Knowledge of viscosity is not only important but a necessity in many industrial and engineering processes. An accurate viscosity data is particularly important in oil and gas industry. For instance, understanding the characteristics of viscosity is necessary in heavy oil production, processing and transportation. As the viscosity of heavy oil is higher than that of a conventional light and medium oils, more energy is required in processing heavy oil resources and usually this requires deploying new set of equipment different from those used to process light and medium oils.

Even though, viscosity of a given fluid can be obtained in two ways, laboratory measurement still remains the primary source of viscosity data. This is because even the so-called viscosity predictive models require reliable laboratory data on representative fluid samples in order to be validated. Therefore, the predictive models in no-way serve as replacement for laboratory measurement despite the expensive and time-consuming nature of the latter.

Owing to the fact that different types of fluids have different viscosity values at different conditions, several viscosity measuring equipment and techniques were developed in the past to suit these different fluids. In the subsequent sections, some of the prominent techniques and equipment are reviewed.

Generally, viscosity measuring instruments (viscometers) can be broadly grouped into two classes namely; primary and secondary viscometers. The primary viscometers are those with a rigorous working equation in which the secondary effects are well characterised, whereas secondary viscometers on the other hand lack the complete description of the secondary fluid mechanisms and hence require accurate correction factors^[2]. In practice, it is often difficult to operate even the so-called primary viscometers in an absolute manner, and as such most of the primary viscometers require calibration with fluids of known viscosity to determine some physical constants. Below is a list of viscometers most commonly used for high-pressure measurement in research laboratories.

1. Capillary viscometers
2. Falling body viscometers
3. Rolling ball viscometers
4. Rotational viscometers
5. Torsional crystal viscometers
6. Oscillating body viscometers

7. Vibrating body viscometers

2.2.1 Capillary viscometers

Capillary viscometers are the oldest and most commonly used for measuring viscosity of Newtonian fluids. In these types of viscometers, measurement is conducted by allowing a known volume of liquid to flow through a fine channel (capillary) and then by monitoring the time taken by the fluid to pass through the two graduation marks in the capillary. The flow rate, along with pressure drop in the capillary and other properties of the fluids allows a direct calculation of viscosity of the sample fluid using the Hagen-Poiseuille's[3] equation as shown in equation (2.5). Capillary viscometers are generally simple in operation and are governed by relatively simple theory and working equations, Figure 2.2 illustrate a simple U-tube capillary viscometer.

Although Capillary viscometers are predominantly used to measure the viscosity of Newtonian fluids, it can as well be used for non-Newtonian fluids. However, in the latter an external force is required to move the liquid through the capillary. For capillary viscometer to work accurately, the following underlying assumptions must be satisfied:

- The flow is parallel to the axis of the capillary i.e. stream line flow pattern lamina
- The flow is steady and there is no acceleration at any point within the tube
- There is no slip at the wall. i.e. the liquid is stationary at the capillary wall
- Newtonian liquid of constant density
- Constant temperature is maintained in the capillary and the increase in temperature due to viscous dissipation is negligible
- The capillary tube is straight and has a uniform cross-section

If all the above assumptions hold, then the general working equation capillary viscometers can be written as follows[4, 5]:

$$\eta = \frac{\pi R^4 \Delta p}{8Q(L + nR)} - \frac{m\rho Q}{8\pi(L + nR)} \quad (2.5)$$

where, R is the radius of the capillary; Δp is the pressure drop across the capillary; $Q = V/t$ is the volumetric flow rate of the fluid in the tube; ρ is the density of the fluid; m is the kinetic energy correction factor; L is the length of the capillary tube and n is the end correction factor

Equation (2.5) relates the viscosity of the fluid to the radius of the capillary tube R , which is difficult to measure directly, usually capillary viscometers are calibrated with fluid of widely known viscosity over wide range of temperatures and flow conditions. Other issues such as wall roughness and non-uniformity of cross section are also eliminated by calibration. Capillary viscometers have been widely used in the past mostly to measure

the viscosity of different liquid samples at atmospheric pressure. However, some high pressure gas capillary viscometers also exist in the literature. For example the gas capillary viscometer developed by Trappenier *et al.*[6] can measure the viscosity of gases at pressures up to 100 MPa. Similarly, a high-temperature capillary viscometer was used to measure the viscosities of noble gases in the temperature range (298.15 to 348.15) K and pressures up to 182 MPa as reported by Trappenier *et al.*[7].

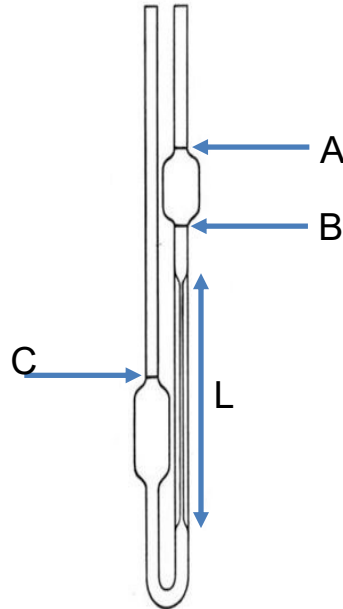


Figure 2.2. U-Tube capillary (Ostwald) viscometer. A and B are the graduation/timing marks, C is the filling mark and L is the length of the capillary

2.2.2 Falling body viscometers

As the name implies, this group of viscometers measures the viscosity of liquid sample by allowing a solid body to fall under gravity through the sample. In principle, the solid body will have a period of acceleration before attaining a uniform terminal velocity. This terminal velocity is achieved when the gravitational force is balanced by the fluid resistance (viscosity) opposing the motion and is determined by noting the terminal velocity of the fallen object.

Although different sizes and shapes can be used for the falling object, however, spherical geometry has been widely used due to its relative simplicity in design and conformance to theory. The theory of falling body viscometer originated from the Stoke's equation given in the following form:

$$6\pi\eta v = \frac{4}{3}\pi r^3(\sigma - \rho)g \quad (2.6)$$

where, η is the viscosity of the fluid; ρ is the density of the fluid; σ is the density of the spherical falling object; r is the radius of the sphere; g is the acceleration due to gravity.

By rearranging equation (2.6) viscosity can be expressed as follows:

$$\therefore \eta = \frac{2gr^2(\sigma - \rho)}{9v\pi} \quad (2.7)$$

In equation 2.7 above, r , σ and ρ are fixed properties of the viscometer and the fluid respectively, whereas the unknown parameter v is obtained from the velocity of the falling body. Equation 2.7 is ideal that takes no account of possible sources of error which is only in principle, but in practice various sources of error exist and should be taken care of. To account for these sources of error, several researchers have proposed different correction factors. For instance, Ladenburg[8] introduced corrections factor that take into account the walls effect and the effect of the depth of the liquid to Stoke's law as shown in equation 2.8 below:

$$\eta_{\text{true}} = \frac{\eta_{\text{measured}}}{(1 + 2.4r/R)(1 + 3.3r/h)} \quad (2.8)$$

here, η_{measured} is the measured viscosity described in equation 2.7 and the term $(1 + 2.4r/R)$ is the correction factor due to wall effect whereas, $(1 + 3.3r/h)$ is a correction factor for the finite depth of the fluid; r is the radius of the sphere; R is the radius of the cylinder and h is the height of the cylinder.

These corrections are both empirical but provide excellent agreement with his observations in the range which he investigated, in which the ratio $r/R < 0.09$ and $r/h < 0.008$ respectively [1, 8, 9].

Besides the spherical geometry, cylindrical geometry is also used as the falling body. This configuration offers an additional advantage in such a way that it can be used to determine the viscosity of both Newtonian and non-Newtonian fluid and has the same working equations as the former. In addition to that, the latter are mostly used for high-pressure systems. For instance, it has been reported in the literature that Dymond *et al* [10] used falling cylinder viscometer to measure the viscosity of pure and mixture of hydrocarbon fluids at pressures up to 500 MPa at a wide range of temperatures.

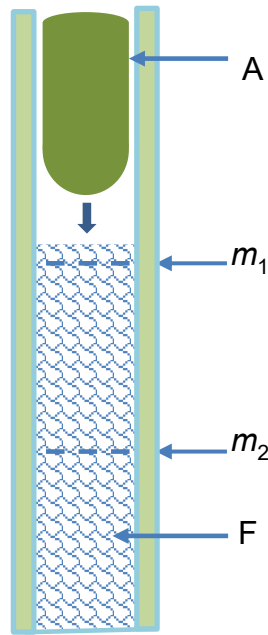


Figure 2.3. Illustration of a simple falling cylinder viscometer. *A*, falling cylinder; m_1 and m_2 timing marks 1 and 2 and *F* is the viscous fluid

2.2.3 Rolling ball viscometer

This type of viscometers are similar both in principle and design to the falling body viscometers except that the cylindrical vessel containing the sample is inclined at an angle θ , and, measurement is made by noting the time taken for a spherical ball to roll down between two points along the slanted plane. Compared to the falling ball viscometers, the rolling ball viscometers offers some advantages including small volume of sample is required, offers visual observation of the rolling ball in both transparent and opaque fluids and flexibility to vary certain parameters such as angle of inclination, rolling distance and tube diameter. Flowers^[11] was the first researcher to introduce the use of rolling ball viscometer in 1915. Subsequently, in 1916 Hersey[12] proposed a new correlation for viscosity measurement using a rolling ball viscometer. In 1943, Hubbard and Brown[13] performed a detailed analysis of the working equations of a rolling ball viscometer for Newtonian fluid. Sage[14] used a rolling ball viscometer to measure the viscosity of hydrocarbon liquids saturated with gases at high pressures. Similarly, Masaya Izuchi and Ken Nishibata[15] developed a high pressure (up to 1GPa) rolling ball viscometer capable of simultaneous density and viscosity measurements by attaching a potentiometric displacement sensor. Paredes *et al.*[16] recently studied the effects of pressure on the viscosity of diisodecyl phthalate using rolling ball viscometer. The general working equation of rolling ball viscometer is given by equation 2.9 below

$$\eta = (k/l)(\rho_0 - \rho)\sin\theta \cdot t \quad (2.9)$$

where, k is a function of the geometry, (diameter ratio of the ball and the tube) also known as calibration coefficient, l and t are the rolling distance and time respectively, ρ_0 and ρ are the densities of the ball and the fluid respectively and θ is the angle of inclination of the cylindrical tube. In equation (2.9), because of the presence of the arbitrary constant k , this types of viscometers requires calibration with fluid of known viscosity to determine the value of k , this qualifies them to be used as secondary viscometers.

Rolling ball viscometers compared to other types of viscometers present a number of uncertainties associated with their operation. Some of these include uncertainty in determining the geometric size (i.e. the diameter of both the tube and the ball), uncertainty in noting the exact rolling time and the angle of inclination of the tube. These uncertainties therefore, limit the accuracy of the device to not better than 3%.

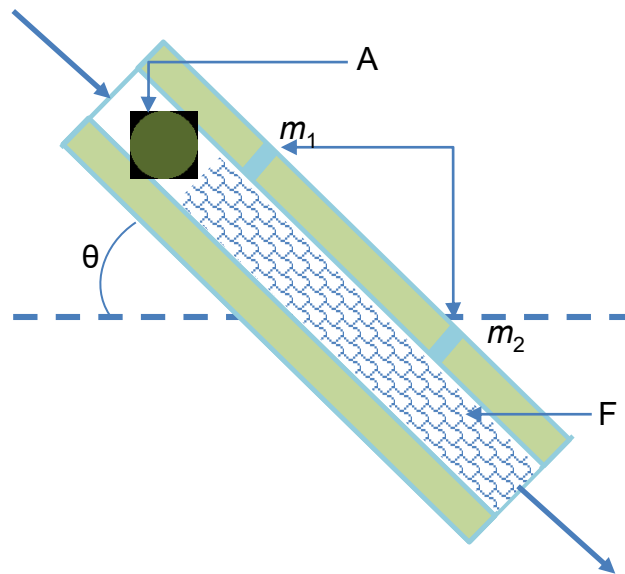


Figure 2.4. Illustration of a simple rolling ball viscometer. A , rolling ball; θ , angle of inclination of the cylinder; m_1 and m_2 are the travelling time sensors and F is the viscous fluid

2.2.4 Rotational viscometer

Rotational viscometers operate on the principle that a force required to rotate an object in a fluid indicate a measure of viscosity of that fluid. In principle, this type of viscometers determines the force required to turn a rotating disc or bob in a fluid at a controlled speed. Rotational viscometers are more elaborate than capillary viscometers. In this type of viscometers, measurement is conducted by filling a cylindrical container of radius R with the sample fluid and the rate of rotation of solid body (usually cylindrical shape) in the fluid is measured. Even though, rotational viscometers are more complex than capillary viscometers, they produce less accurate measurements especially for Newtonian fluids^[1]. However, in contrast to the latter, rotational viscometers offers an advantage of carrying

out measurement at steady state conditions as well as performing continuous measurement on sample fluids. Rotational viscometers are available in different design and configurations and generally available in two main categories namely - (i) the Synchronous (stepper) motor / spring and; (ii) the Servomotor /digital encoder. Figure 2.5 shows a schematic of a synchronous rotational viscometer.

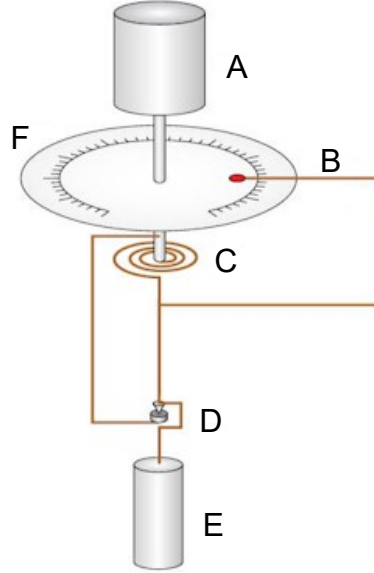


Figure 2.5. Schematic of a synchronous rotational viscometer: A. synchronous motor, B. pointer or capacitive sensor, C. spring, D. pivot, E. rotor and F. dial

Fundamentally, rotational viscometers measure the torque M , of a fluid via strain gauge on a fixed surface between two rotationally symmetric surfaces arranged coaxially with one of them rotating at constant angular velocity ω and the gap between these surfaces is filled with fluid under test. The cone-and-plate rotational viscometers are governed by the following working equation[17].

$$\eta = \frac{3\alpha M}{2\pi\omega r^3} \quad (2.10)$$

where, M is the torque, r is the radius of the cone base, ω , is the angular velocity and α is the cone base angle.

Equation 2.10 is applicable to rotational viscometers with smaller cone angles typically $\alpha < 3^\circ$ simply because of shear rate which is essentially constant for constant values of ω . For the concentric-cylinder rotational viscometers, the working equation is slightly modified to take into account the radii of the inner and outer cylinders as shown in equation 2.11 below.

$$\eta = \frac{M}{4\pi\omega l} \left(\frac{1}{r_i^2} - \frac{1}{r_o^2} \right) \quad (2.11)$$

here, l is the length of the cylinders

Equations 2.10 and 2.11 are not exact and often require the use of correction factors to improve their accuracies. Walters *et al.*[18] performed a rigorous mathematical analysis and determined these corrections terms for different geometries.

2.2.5 Torsional crystal viscometer

This type of viscometer makes use of piezoelectric material immersed in a fluid sample and set into torsional vibration by the passage of alternating current (ac) through its axis. The resonance frequency and bandwidth of the vibration are respectively related to the density and viscosity of the surrounding fluid. It was discovered that the resonance frequency as well as the bandwidth of the vibration of material in a given fluid differ significantly from their corresponding values in vacuum due to the density and viscosity difference between the two media. Therefore in order to use this device, measurement is first made in vacuum to determine the resonance frequency in vacuum and the viscosity can be obtained from the following relation.

$$\eta = \pi \left(\frac{f_r}{\rho} \right) \left(\frac{m}{S} \right)^2 \left(\frac{f_{br}}{f_r} - \frac{f_{bvac}}{f_{vac}} \right)^2 \quad (2.12)$$

where, f_r and f_{vac} are the resonance frequencies of the vibration of the material in the fluid and in vacuum respectively, m and S are the mass and surface area of the crystal material respectively. f_{br} and $f_{b,vac}$ are the bandwidth of the vibration in the fluid and in vacuum respectively. Because of the fact that measurement/calibration in vacuum is required in the use of these viscometers, they are therefore, considered as secondary viscometers. Torsional crystal viscometer was first developed by Mason *et al.*[19, 20] in 1947 for low temperature applications, however, subsequent researchers such as Diller and Frederick[21] developed a torsional crystal viscometer rated for application at extended temperatures up to 600 K.

2.2.6 Oscillating body viscometer

Oscillating body viscometers consist of solid object usually spherical, cylindrical or cup dipped in a cylindrical tube containing the fluid sample. Viscosity measurement is made by allowing the solid body to oscillate within the bulk of the fluid. The fluid exerts a viscous drag on the oscillating body causing a marked difference in the observed natural frequencies (f) as well as the damping coefficients (Δ) of the oscillation in the fluid and in vacuum. The magnitude of the change depends on the viscosity and density of the fluid in addition to some properties (e.g. radius of the oscillating body). The working equation of the oscillating body viscometer was described by Newel *et al.*[22] and Wakeham *et al.*[4] as shown below:

$$(S + \Delta_0)^2 + 1 + D(S) = 0 \quad (2.13)$$

where, $D(S)$ is the torque acting on the oscillating body.

Oscillating body viscometers produce accurate viscosity results provided accurate density values are available. Kestin J., and Leidenfrost W.[23] in 1959 developed the first oscillating-disk viscometer for measuring the viscosity of gases near room temperature and pressures up to 60 MPa with an estimated uncertainty of about 0.1 %. Subsequently, many researchers developed different types of oscillating-body viscometers for different types of fluids. Knapstad *et al.*[24] used oscillating-cup viscometer to measure the viscosity of many pure hydrocarbons in the temperature range of (20 to 150) °C within an estimated experimental uncertainty of 0.33 to 0.56 %.

2.2.7 Vibrating object viscometer

This category of viscometers operates in a similar way to the oscillating-body viscometers. However, in vibrating viscometers the vibrating element is set to transverse oscillation due to the passage of electric current through it in the presence of magnetic field. The frequency of oscillation of the vibrating element and the width of the resonance peak are respectively related to the density and viscosity of the surrounding fluid[25]. Vibrating viscometer has some advantages over the oscillating-body viscometers, these include simple design and usually smaller in size which requires small volume of sample fluid thereby making it easier to perform measurement at extreme temperatures and pressures. Vibrating-wire viscometer is particularly a simple type of vibrating viscometers, in which a thin circular section wire is tensioned and dipped into the cylinder containing the sample fluid. In order to obtain the viscosity of the fluid sample using vibrating viscometers usually calibration of the device in both no density medium (vacuum) and fluid of known viscosity is required so as to determine the values of some physical constants in the working equations. In this project, vibrating-wire device was used and its characteristics are extensively discussed in the subsequent chapter.

2.2.8 Summary

As mentioned in the opening of this chapter, different fluids have different viscosity characteristics at different conditions. In other word, choosing a viscometer would require consideration of the following key factors: i). nature of the fluid, ii). the intended temperature, and pressure of application, iii) sample size, iv) Ease of use and iv) the accuracy required in the intended measurement. Table 2.1 summarises some of these factors for some high-pressure viscometers discussed above based on the literature data presented in Table 2.2. Furthermore, some of the viscometers has some advantages over others in terms flexibility in design and operations; some can be used in absolute sense,

while others require calibration to determine some physical parameters. In general, the choice of a viscometer would be dictated by the factors highlighted above.

Table 2.1: Summary of some factors considered in chosen a viscometer

	Capillary	Rolling Ball	Oscillating	Vibrating
Accuracy %	1 to 2	2 to 3	0.3 to 1	1 to 3
High Temp. K	473	403	436	473
High pres. MPa	48	100	40	200
Calibration	required	required	required	*Not required
Density input	required	required	required	#Not required
Ease of use	easy	easy	moderate	complex
Sample size	small	small	small	medium

*If operated in absolute mode, #can provide simultaneous accurate density and viscosity result

2.3 Review of literature viscosity data of hydrocarbon mixtures with light gases

Since the present work involved the study of viscosity and density of mixtures of hydrocarbon with light gases, it is important to conduct a thorough search on the available viscosity data for the relevant mixtures in the literature. This is necessary in order not to repeat any previous work except for the purpose of validating the measurement technique and also it would help in identifying the gaps in the viscosity data in the literature. For this reason, a complete and comprehensive database of available viscosity data of relevant asymmetric hydrocarbon mixtures was compiled as shown in Table 2.1. Although the present study involved asymmetric mixtures of methane + hydrocarbons, however the available data on the complementary asymmetric systems of CO₂ + hydrocarbons were also included in the table to illustrate the data scarcity of these types of systems in the literature. From the table, it is evident that there is a paucity of viscosity data especially for the highly asymmetric mixtures in both cases.

Similarly, from the modelling point of view, previous work by Ciotta *et al.*[26, 27] pointed out that the hard sphere model and the VW models have the potentials to predict the viscosity of asymmetric mixtures. In this regards, we tested the performances of these two models on some the literature data in Table 2.1. For instance, it can be seen from the table that the moderately asymmetric system of methane + decane has been studied independently by eight authors and the most of the data are in agreement within their mutual experimental uncertainties except for the two authors. As can be seen in Table 4.2 in chapter 4, our analysis revealed that both models reproduced the experimental viscosities from the following sources namely: Peleties, *et al.*[28], Audonnet, *et al.*[29], Canet, *et al.*[30], Daridon, *et al.*[31], Knapstad, *et al.*[32] and Dauge, *et al.*[33], with $\Delta AARD, \eta$ consistently less than 4 %. However, the large deviations shown in the last two

studies, the Gozalpour, *et al.*[34] and Lee, *et al.*[35] were not surprising as the experimental results from the latter deviated significantly from the results of other researchers. For instance, Knasptad *et al.*[32] reported that Lee's results deviated as much as 45 % from their results. For Gozalpour's results, the higher deviations in viscosity were attributed to the fact that the author claimed that the measurements were conducted near the critical point at which they observed up to 10 % viscosity increment upon approaching the saturation pressure of the mixture. Although this analysis was conducted on moderately asymmetric systems, nevertheless, it highlights the potentials of these models on predicting the viscosity of highly asymmetric mixtures.

Table 2.1: Viscosity of asymmetric hydrocarbon mixtures

ref.	fluids	T /K	p /MPa	x_1	Points	methd	U_η^*
Simple asymmetric liquid mixtures							
[36]	C_8+C_{12}	298 to 473	200	0.434 to 1	228	VW	2%
[37]	C_6+C_{16}	298.15	0.101	0 to 1	11	UBV	1%
Asymmetric mixtures of CH_4+hydrocarbons							
[38]	C_1+C_6	293 to 390	41	0.359 to 0.749	42	UN	UN
[39]	C_1+C_{10}	298 to 393	75	0.00 to 0.429	243	VW	2%
[29]	C_1+C_{10}	303 to 393	75	0.00 to 0.799	144	VW	3%
[30]	C_1+C_{10}	293 to 373	140	0.3124 to 0.7566	295	FB	3%
[32]	C_1+C_{10}	293 to 423	40	0.00 to 0.8467	133	OV	1.8%
[33]	C_1+C_{10}	393.15	140	0.3124	65	FB	3%
[31]	C_1+C_{10}	303 to 313	10 to 80	0.227 to 0.3124	15	CR	-
[34]	C_1+C_{10}	310.95	34 to 38	0.8064 to 0.9514	20	CT	3%
[35]	C_1+C_{10}	310 to 444	48.263	0.3 to 0.7	71	CT	3%
[17]	C_1+C_{10}	310 to 344	10.34 to 32.75	0.364 to 0.781	6	UN	UN
[17]	C_1+C_{16}	305 to 333	0.1 to 55.16	0.00 to 0.856	16	UN	UN
Other binary asymmetric mixtures							
[40]	C_1+cC_6	295 to 443	10.2 to 40.8	0.2 to 0.57	57	OC	1%
[41]	C_7+C_{20}	293 to 343	0.1	0 to 1	34	RB	3%
[41]	C_7+C_{22}	303 to 343	0.1	0 to 1	27	RB	3%
[41]	C_7+C_{24}	313 to 343	0.1	0 to 1	21	RB	3%
[41]	$C_{16}+C_{20}$	293 to 343	0.1	0 to 1	35	RB	3%
Ternary asymmetric hydrocarbon mixtures							
[36]	$C_3+C_8+C_{12}$	298 to 473	100	0.00 to 0.425	206	VW	2%

[41]	$C_7+C_{20}+C_{24}$	303 to 343	0.1	$0 \leq x_{20} \leq 0.5$ $0 \leq x_{24} \leq 0.5$	26	RB	3%
Asymmetric mixtures of CO₂+hydrocarbons							
[42]	$CO_2+C_2+C_3+C_4$	298 to 468	0.1	0.2 to 0.8		OD	0.3%
[43]	CO_2+C_{10}	310 to 403	6 to 12	0.15 to 0.50		RB	3%
[44]	CO_2+C_{10}	310 to 403	7 to 30	0.15 to 0.85		CT	2%
[27]	CO_2+C_{16}	298 to 473	120	0.0 to 0.727	136	VW	2%
[26]	$CO_2+bC_{30}H_{62}$	303 to 448	170	0.423 to 0.788		VW	2%
[45]	$CO_2+bC_{30}H_{62}$	293 to 353	0.1 to 30	0 to 0.417		RB	2%
[43]	$CO_2+C_5+C_6+C_7+C_{10}$	323 to 423	2 to 5	0.08 to 0.22		RB	3%

Table 2.2: Density of asymmetric hydrocarbon mixtures

ref.	fluids	T /K	p /MPa	x_1	Points	methd	U_p^* %
Asymmetric mixture of C_1+C_{10}							
[29]	C_1+C_{10}	298 to 393	75	0.00 to 0.799	144	VW	0.2
[30]	C_1+C_{10}	293 to 373	140	0.3124 to 0.7566	295	VT	0.13
[33]	C_1+C_{10}	393.15	140	0.3124	65		
Asymmetric mixture of C_1+C_{14}							
[46]	C_1+C_{14}	295 to 448	10	0 to 0.4	24	VT	0.1
[47]	C_1+C_{14}	313 to 433	80 to 200	0.102 to 0.664	74		
Asymmetric mixture of C_1+C_{18}							
[48]	C_1+C_{18}	323 to 447	0.19 to 10	0 to 0.4	24	VT	0.1
Other asymmetric mixtures							
[41]	C_7+C_{20}	293 to 343	0.1	0 to 1	34	VT	0.1
[41]	C_7+C_{22}	303 to 343	0.1	0 to 1	27	VT	0.1
[41]	C_7+C_{24}	313 to 343	0.1	0 to 1	21	VT	0.1
[41]	$C_{16}+C_{20}$	293 to 343	0.1	0 to 1	35	VT	0.1
Ternary asymmetric mixtures							
[41]	$C_7+C_{20}+C_{24}$	303 to 343	0.1	$0 \leq x_{20} \leq 0.5$ $0 \leq x_{24} \leq 0.5$	28	VT	0.1

CR: Quartz crystal resonator

CT: Capillary tube viscometer

FB: Falling body viscometer

OD: Oscillating disc

FB: Falling body viscometer

RB: Rolling ball viscometer

CT: Capillary tube viscometer

 x_1 is the mole fraction of the first named component U^* Claimed authors' experimental uncertainties

OV: Oscillating vessel

CV: Cylindrical vessel viscometer

VW: Vibrating-wire viscometer

UBV: Ubbelohde viscometer

OV: Oscillating cup

CR: Quartz crystal resonator

VT – Anton Paar Vibrating u-tube densimeter

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Vibrating-wire Viscometry

3.1 Introduction

Historically, the principle of vibrating-wire viscometer emanated from the early studies on the vibration of a simple pendulum. In 1820, Bessel[1] described the change in period of the vibration of a wire when in air and that of vacuum and attributed the differences to the inertial and buoyancy effect of air. Subsequently, it was discovered that viscosity also contributed immensely to the observed increase in the period of vibration of the wire in air. Stokes[2] in 1850 described a relationship between the viscosity of the surrounding fluid and the period of vibration of the wire. Tough *et al.*[3, 4] in 1960 developed the first vibrating wire device and used it to measure the viscosity of helium at very low temperatures. Soon after the invention of the first practical device, research in the vibrating wire technique has been receiving considerable attention and different modifications in both the theory and design were performed. For example, in 1986, a team of researchers lead by Retsina *et al.*[5, 6], reviewed the theory governing the motion of vibrating wire performing transverse oscillation in a fluid. Their review incorporated the effect of the wire stiffness, the mechanics of the fluid surrounding the wire and the mechanical motion of the vibrating wire. This development leads to better understanding of the theory of the vibrating-wire device and also stimulate the derivation of a more complete working equation for the practical device as highlighted in the subsequent sections.

3.2 Theory of vibrating-wire device

The theory of vibrating wire viscometer was based on the understanding of the well-founded working equations with clear practical constrains. It is fundamentally based on measurement of resonance frequency of a cylindrical tube performing steady transverse oscillation in a fluid as described by Retsina *et al.*[6] the theory followed the analysis of the mechanical motion of the wire coupled with the understanding of the mechanics of the surrounding fluid. The complete working equation was derived by recognising both the theoretical and practical constrains of the device[7]. In the subsequent section, the detailed derivation of the complete working equation will be highlighted.

3.3 The mechanical motion of the wire

The equations describing the mechanical motion of the wire were fundamentally based on the elastic beam theory transformed into mathematical models. This transformation was achieved by making the following governing assumptions [5, 6]. That the beam is;

- an elastic solid body with its length much greater than its thickness
- prismatic (i.e. the cross sections are the same in all respect)
- homogeneous (with constant material characteristics)

- straight with its axes forms a part of a straight line
- untwisted (i.e. the principal axes of elasticity are evenly directed in space)

Considering the above assumptions, the classical beam theory of Euler-Bernoulli[8] is the most appropriate mathematical model to describe the motion of this type of beam. The model primarily described the simple lateral vibration of the beam with further assumptions of negligible shear deformation and rotational inertia as against the prevailing bending deformation and translational inertia.

3.3.1 Simple lateral vibration of the wire

According to the Euler-Bernoulli theory, the lateral vibration of the beam in the yz plane occurs if the deflection $U(z, t)$ is only attributed to the bending moment. Figure 3.1 illustrates a typical Euler-Bernoulli beam,

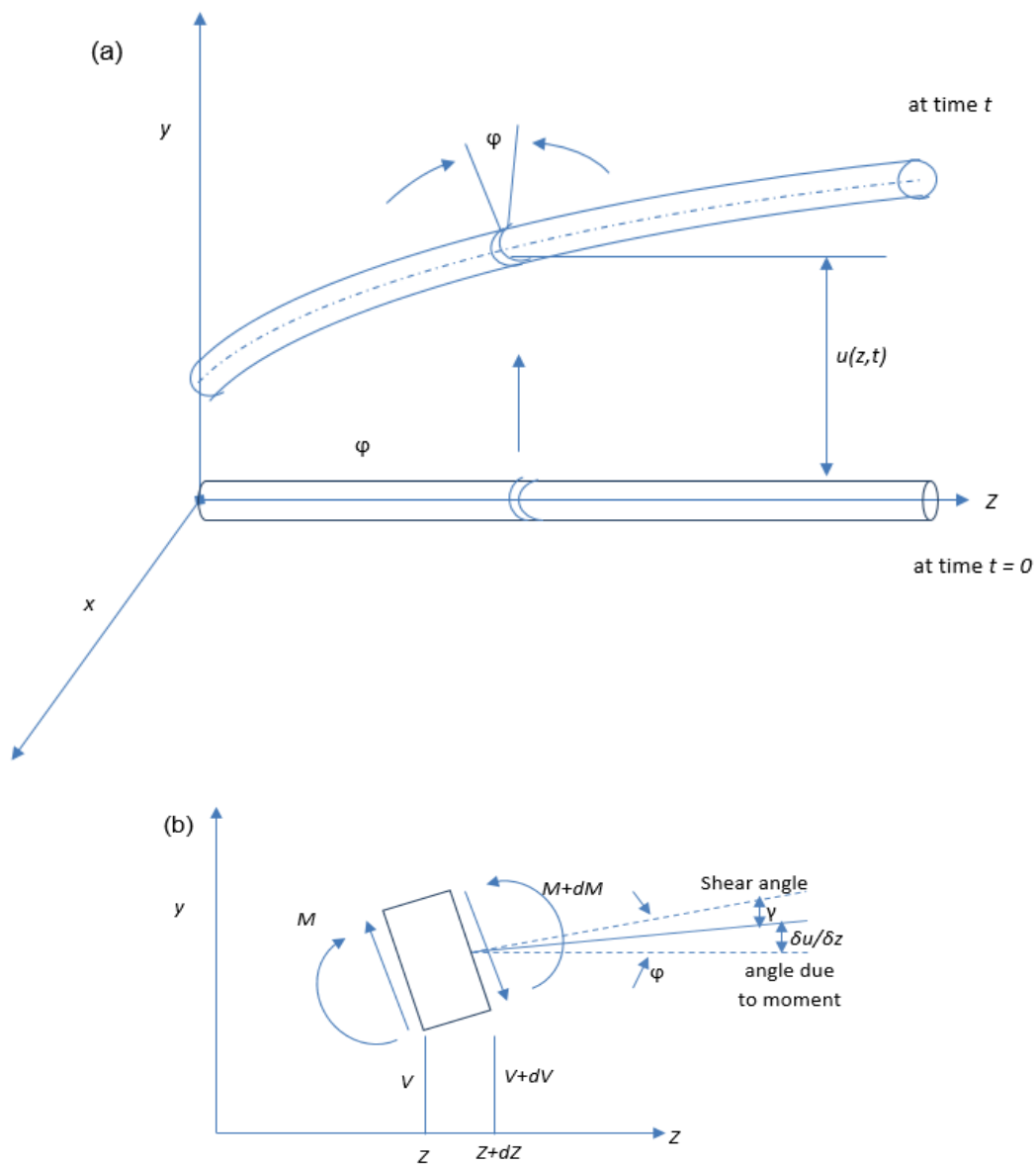


Figure 3.1(a) Flexural behaviour, and (b) dynamic forces on a straight beam in the yz plane^[9]

for such type of beam, the rotational movement around the x-plane and the displacement U , in the y-direction are related according to the following expression;

$$\phi_x = \frac{\partial u}{\partial z} \quad (3.1)$$

analysis of the dynamic forces acting on the elements resulted in the following equation

$$m_s \frac{\partial^2 u}{\partial t^2} \partial z = V - \left(\frac{\partial V}{\partial z} \partial z + V \right) \quad (3.2)$$

and the inertia force equation is given by;

$$m_s \frac{\partial^2 u}{\partial t^2} = - \frac{\partial V}{\partial z} \quad (3.3)$$

where V is the shear force, and m_s mass per unit length of the beam

by taking moment balance across any point to the right i.e. $(z + \partial z)$, the following was obtained;

$$\frac{\partial M}{\partial z} \partial z = V \partial z \quad (3.4)$$

$$\therefore V = \frac{\partial M}{\partial z} \quad (3.5)$$

substituting for V in equation 3.4, results in;

$$m_s \frac{\partial^2 u}{\partial t^2} = - \frac{\partial^2 M}{\partial z^2} \quad (3.6)$$

recalled from the basic strength of material that, the moment of a wire material is related to its curvature by:

$$M = EI_a \frac{\partial^2 u}{\partial z^2} \quad (3.7)$$

where, E is the Young's modulus of elasticity, I_a is the second moment of inertia

by substituting equation 3.7 for M , equation 3.6, yields:

$$m_s \frac{\partial^2 u}{\partial t^2} = - \frac{\partial^2}{\partial z^2} \left(EI_a \frac{\partial^2 u}{\partial z^2} \right) \quad (3.8)$$

Where the term EI_a is constant and it is a measure of flexural stress of the wire, therefore it can be factored out of the differential term of equation 3.8 and can be re-written as

$$EI_a \frac{\partial^4 u}{\partial z^4} + m_s \frac{\partial^2 u}{\partial t^2} = 0 \quad (3.9)$$

Equation 3.9 described the flexural behaviour of a beam/wire under bending moment with the assumption of negligible rotary inertia and shear deformation and with no axial loading attached to it. However, in both cases of vibrating wire designs (i.e. BM or 2C), the wire is subjected to loading. For example in the case of BM, the wire is positioned in a vertical plane with a suspended buoyant mass attached at the lower end thereby subjecting it to the axial tension. Similarly, in the design of the so-called 2C vibrating wire, the wire is pre-tensioned before clamping at both ends. Consequently, in the next section we are going to consider the effect of axial tension on the wire.

3.3.2 Effect of axial loading

The mechanics of the wire under axial tension can be described by using taut string behaviour^[6] as shown in the Figures 3.2(a) and (b) below,

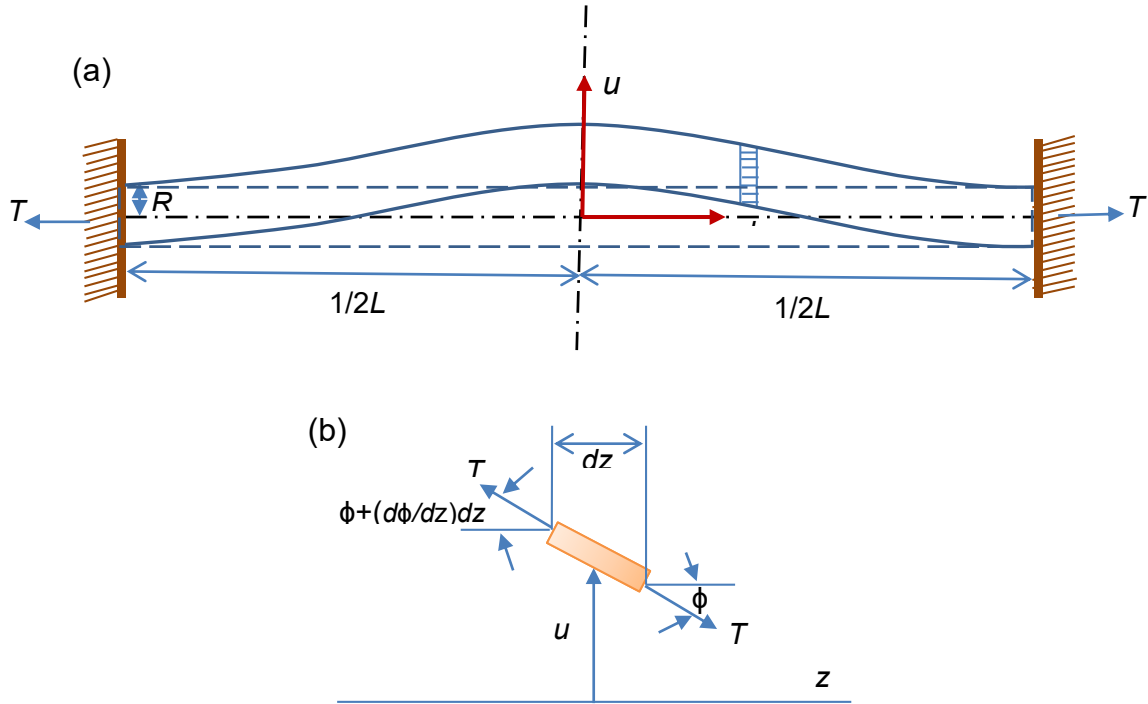


Figure 3.2 (a) Lateral vibration of the wire (b) small element under axial forces^[6]

the lateral deflection u can be related to position and time. So, by Newton's law of motion, the rotation around the x-plane is proportional to the deflection u and is given by the following expression:

$$m_s \frac{\partial^2 u}{\partial t^2} dz = T \left(\phi + \frac{\partial \phi}{\partial z} dz \right) - T \phi. \quad (3.10)$$

In practice, the stiffness of the wire cannot be negligible as assumed earlier, therefore by incorporating it into the system, equation 3.10 becomes:

$$m_s \frac{\partial^2 u}{\partial t^2} dz = T \left(\varphi + \frac{\partial \varphi}{\partial z} dz \right) - T \varphi - \left(V + \frac{\partial V}{\partial z} dz \right) + V, \quad (3.11)$$

on further simplifications, equation 3.11 reduces to:

$$m_s \frac{\partial^2 u}{\partial t^2} = T \frac{\partial^2 u}{\partial z^2} - \frac{\partial V}{\partial z} \quad (3.12)$$

putting $V = \frac{\partial M}{\partial z}$ and $M = EI_a \frac{\partial^2 u}{\partial z^2}$, equation 3.12 becomes

$$m_s \frac{\partial^2 u}{\partial t^2} = T \frac{\partial^2 u}{\partial z^2} - \frac{\partial^2}{\partial z^2} \left(EI_a \frac{\partial^2 u}{\partial z^2} \right) \quad (3.13)$$

again, since the term EI_a is constant, then equation 3.13 can be re-expressed as follows:

$$EI_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + m_s \frac{\partial^2 u}{\partial t^2} = 0 \quad (3.14)$$

Equation 3.14 describes the motion of vibrating-wire under axial tension but without consideration of rotary inertia and shear deformation effects. In practice, the vibration of the wire is however significantly affected by these effects, and is therefore considered in the subsequent sections.

3.3.3 Effects of rotary inertia and shear deformation

In contrast to the Euler-Bernoulli beam, the Timoshenko[10] beam accommodates the effects of shear deformation on the beam. According to this theory, the slope of the centre line of the beam will reduce substantially due to the shear angle and hence equation 3.1 can be re-written as:

$$\varphi - \gamma = \frac{\partial u}{\partial z} \quad (3.15)$$

and the shear deformation effect γ can be estimated from:

$$\gamma = \frac{V}{\chi AG} \quad (3.16)$$

where χ is a shape factor which for a circular beam can be taken as 0.9 as reported by Cowper^[11], A is the cross sectional area and G is the modulus of elasticity and the wire curvature φ can be evaluated from the following relation:

$$\frac{\partial \varphi}{\partial z} = \frac{M}{EI_a} \quad (3.17)$$

by incorporating the rotary inertia terms, the dynamic moment equation can be written as:

$$J \frac{\partial^2 \varphi}{\partial t^2} = \frac{\partial M}{\partial z} - V \quad (3.18)$$

by combining the dynamic force equation 3.14 and the dynamic moment equations 3.15 to 3.18 together, the equilibrium equation for translational motion in the y -plane and the rotational motion about the x -plane can be obtained as:

$$El_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + m_s \frac{\partial^2 u}{\partial t^2} - \left(J + \frac{El_a m_s}{\chi AG} \right) \frac{\partial^4 u}{\partial z^2 \partial t^2} + \frac{J m_s}{\chi AG} \frac{\partial^4 u}{\partial t^4} = 0 \quad (3.19)$$

Putting $m_s = A\rho_s$ and $J = I\rho_s$ (where ρ_s is the density of the wire), the equation for free oscillation can be written as

$$El_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + m_s \frac{\partial^2 u}{\partial t^2} - \rho_s I_a \left(1 + \frac{E}{\chi G} \right) \frac{\partial^4 u}{\partial z^2 \partial t^2} + \frac{\rho_s^2 I}{\chi G} \frac{\partial^4 u}{\partial t^4} = 0 \quad (3.20)$$

where, the last two terms account for the correction due to the shear deformation and rotary inertia effects respectively.

For a situation whereby the wire performs a periodic oscillation due to the effect of externally applied force, equation 3.20 can be re-expressed as follows;

$$El_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + m_s \frac{\partial^2 u}{\partial t^2} - \rho_s I_a \left(1 + \frac{E}{\chi G} \right) \frac{\partial^4 u}{\partial z^2 \partial t^2} + \frac{\rho_s^2 I}{\chi G} \frac{\partial^4 u}{\partial t^4} = F(z, t) e^{i\omega t} \quad (3.21)$$

where $F(z, t) e^{i\omega t}$ is the applied force per unit length and ω is the angular frequency of the oscillation.

3.4 The effect of the surrounding fluid

Analysis of the sampled signal/voltages revealed that the natural frequency of oscillation of the wire differs considerably in different medium. For instance the frequency observed in vacuum significantly differs from that obtained in a given fluid. The two frequencies differ in the width of the resonance peak as well as in the resonance frequency. While the former is attributed to the viscous effect of the fluid, the latter is as a result of the density difference between the two media. To account for these variations, the equation of the wire should be modified to incorporate some additional parameters such as m_s to account for the added mass due to density of the fluid and D_f to account for the additional drag due to the internal damping of the wire material D_0 . Hence equation 3.21 can be re-written to give the more complete form in presence of any given fluid as;

$$El_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + (m_s + m_f) \frac{\partial^2 u}{\partial t^2} + (D_f + D_0) \frac{\partial u}{\partial t} - \rho_s I_a \left(1 + \frac{E}{\chi G} \right) \frac{\partial^4 u}{\partial z^2 \partial t^2} + \frac{\rho_s^2 I}{\chi G} \frac{\partial^4 u}{\partial t^4} = F(z, t) e^{i\omega t} \quad (3.22)$$

As the length of the wire is much larger than its radius (i.e. $L \gg R$), the shear deformation effects can be assumed to be negligible. Similarly, the rotary inertia term can be

neglected provided that the displacement u of the wire is small and hence equation 3.22 can be reduce to following form;

$$EI_a \frac{\partial^4 u}{\partial z^4} - T \frac{\partial^2 u}{\partial z^2} + (m_s + m_f) \frac{\partial^2 u}{\partial t^2} + (D_f + D_0) \frac{\partial u}{\partial t} = F(z, t) e^{i\omega t} \quad (3.23)$$

where the terms in equation 3.23 have the following definitions

$$I_a = \frac{1}{2} \pi R^4$$

is the second moment of area

$$m_s = \rho_s \pi R^2$$

is the mass per unit length of the wire

$$m_s = \rho_s \pi R^2 k$$

is the added mass to the wire by the surrounding fluid

$$D_0 = 2\pi\omega R^2 \rho_s \Delta_0$$

is the internal damping of the wire

$$D_f = \rho \pi \omega R^2 k$$

is the added damping due to the fluid surrounding the wire

Δ_0 is the damping coefficient obtained from measurement in vacuum, and the parameters k and k' are frequency functions of the oscillation obtained from analysis of the fluid mechanics as discussed in the following section.

3.4.1 Analysis of the fluid mechanics

The detail derivations of the mechanics of the fluid surrounding the vibrating-wire sensor can be found elsewhere [5, 6]. Nevertheless, the assumptions made and constrains involved in deriving the equations would be highlighted in this section.

Firstly, it was assumed in the derivation of the equations that the wire is infinitely long compared to its radius (i.e. $L \gg R$), and that the radius of the container R_c coincides with the position of the wire at rest as shown in Figure 3.3.

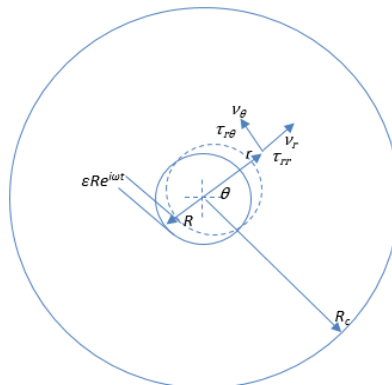


Figure 3.3: Vibrating-wire radius R enclosed in a cylindrical container of radius R_c coincident with the position of the wire at rest[6]

For simplicity of analysis, the boundary conditions for the wire clamped at both ends (2C) would be adopted and subsequently would be corrected to reflect the approximate equation to be applied to vibrating wire viscometer with a suspended mass (BM). For the kind of viscometer shown in Figure 3.3, the fluid motion would be in the $r - \theta$ direction. Again, assuming the fluid is incompressible so that the match number $M_a \ll 1$, i.e.

$$M_a = \frac{\omega \varepsilon R}{c} \ll 1 \quad (3.24)$$

where c , is the speed of sound in the fluid, ε is the dimensionless amplitude of oscillation giving by $\varepsilon = u/R$ with u as the wire displacement, and R as the wire radius.

The mass conservation equation can be obtained by combining the gravitational effect and the pressure terms as follows;

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} = 0 \quad (3.25)$$

the radial momentum conservation equation can be written as;

$$\begin{aligned} \rho \left[\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} \right] = \\ - \frac{\partial p}{\partial r} + \eta \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_r) \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} \right] \end{aligned} \quad (3.26)$$

Similarly, the corresponding angular momentum conservation equation is;

$$\begin{aligned} \rho \left[\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} - \frac{v_r v_\theta}{r} \right] = \\ - \frac{1}{r} \frac{\partial p}{\partial \theta} + \eta \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right) + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} \right] \end{aligned} \quad (3.27)$$

v_r and v_θ are the coefficients of fluid velocities for the angular and the radial direction and can be evaluated from

$$v_r = i\omega R \varepsilon e^{i\omega t} \cos \theta \quad (3.28)$$

and

$$v_\theta = -i\omega R \varepsilon e^{i\omega t} \sin \theta \quad (3.29)$$

at

$$r = R \varepsilon e^{i\omega t} \cos \theta + R \sqrt{1 - \varepsilon^2} e^{2i\omega t} \sin^2 \theta \quad (3.30)$$

and when the wire is at rest,

$$v_r = v_\theta = 0 \text{ at } r = R_c \quad (3.31)$$

These conditions represent the position of the wire as illustrated in Figure 3.3

Again, both v_r and v_θ can be effectively related to the stream function ψ as follows

$$v_r = \frac{1}{r} \frac{\partial \psi}{\partial \theta}, \quad v_\theta = -\frac{1}{r} \frac{\partial \psi}{\partial r} \quad (3.32)$$

Equation 3.26 and 3.27 can be combined together to obtain a more general expression for ψ by cross differentiation with respect to both r and θ as follows;

$$\begin{aligned} & \frac{1}{\sigma} \frac{\partial^3 \Phi}{\partial \theta^2 \partial \tilde{\tau}} + \frac{\partial^2 \Phi}{\partial \sigma \partial \tilde{\tau}} + \sigma \frac{\partial^3 \Phi}{\partial \sigma^2 \partial \tilde{\tau}} + \varepsilon \Omega \left[\frac{1}{\sigma^2} \frac{\partial \Phi}{\partial \theta} \frac{\partial^3 \Phi}{\partial \sigma \partial \theta^2} - \frac{2}{\sigma^3} \frac{\partial^2 \Phi}{\partial \theta^2} \frac{\partial \Phi}{\partial \theta} \right. \\ & - \frac{1}{\sigma^2} \frac{\partial \Phi}{\partial \sigma} \frac{\partial^3 \Phi}{\partial \theta^3} - \frac{1}{\sigma} \frac{\partial^2 \Phi}{\partial \sigma \partial \theta} \frac{\partial \Phi}{\partial \sigma} + \frac{\partial \Phi}{\partial \theta} \frac{\partial^3 \Phi}{\partial \sigma^3} - \frac{\partial \Phi}{\partial \sigma} \frac{\partial^3 \Phi}{\partial \sigma^2 \partial \theta} + \frac{1}{\sigma} \frac{\partial \Phi}{\partial \theta} \frac{\partial^2 \Phi}{\partial \sigma^2} \\ & \left. - \frac{1}{\sigma^2} \frac{\partial \Phi}{\partial \theta} \frac{\partial \Phi}{\partial \sigma} \right] = \frac{2}{\sigma} \frac{\partial^4 \Phi}{\partial \theta^2 \partial \sigma^2} - \frac{2}{\sigma^2} \frac{\partial^3 \Phi}{\partial \sigma \partial \theta^2} + \frac{1}{\sigma^3} \frac{\partial^4 \Phi}{\partial \theta^4} + 2 \frac{\partial^3 \Phi}{\partial \sigma^3} + \sigma \frac{\partial^4 \Phi}{\partial \sigma^4} \\ & - \frac{1}{\sigma} \frac{\partial^2 \Phi}{\partial \sigma^2} + \frac{1}{\sigma^2} \frac{\partial \Phi}{\partial \sigma} + \frac{4}{\sigma^3} \frac{\partial^2 \Phi}{\partial \theta^2} \end{aligned} \quad (3.33)$$

where, the dimensionless groups in the equation 3.33 above can be defined in the following way

for the stream function: $\Phi = \frac{\psi}{\varepsilon \omega R^2},$

for frequency based on ρ : $\Omega = \frac{\rho \omega R^2}{\eta},$

for radius of the container: $\sigma^* = \frac{R_c}{R}, \quad (3.34)$

for radial coordinates: $\sigma = \frac{r}{R},$

and time: $\tilde{\tau} = \frac{t \eta}{\rho R^2}.$

The dimensionless group Ω can be related to Reynold's number, since the Reynolds number can be expressed as a ratio of inertia to viscous forces, thus $R_e = \rho \omega \varepsilon R^2 / \eta$, and the dimensionless quantity Ω in equations 3.33 and 3.34.

The non-linear inertial effect term in equation 3.33 can be neglected on the assumption that the Reynolds number due to the wire displacement is very small. However, the corresponding linear inertial can still be retained. Consequently, the solution to the equation is valid within certain range of values for both R_e and Ω , typically:

$$R_e \approx \varepsilon \ll 1, \quad \Omega \approx 1 \quad (3.35)$$

Therefore, equation 3.33 reduces to:

$$\begin{aligned} \frac{1}{\sigma} \frac{\partial^3 \Phi}{\partial \theta^2 \partial \tilde{\tau}} + \frac{\partial^2 \Phi}{\partial \sigma \partial \tilde{\tau}} + \sigma \frac{\partial^3 \Phi}{\partial \sigma^2 \partial \tilde{\tau}} &= \frac{2}{\sigma} \frac{\partial^4 \Phi}{\partial \theta^2 \partial \sigma^2} - \frac{2}{\sigma^2} \frac{\partial^3 \Phi}{\partial \sigma \partial \theta^2} + \frac{1}{\sigma^3} \frac{\partial^4 \Phi}{\partial \theta^4} \\ + 2 \frac{\partial^3 \Phi}{\partial \sigma^3} + \sigma \frac{\partial^4 \Phi}{\partial \sigma^4} - \frac{1}{\sigma} \frac{\partial^2 \Phi}{\partial \sigma^2} + \frac{1}{\sigma^2} \frac{\partial \Phi}{\partial \sigma} + \frac{4}{\sigma^3} \frac{\partial^2 \Phi}{\partial \theta^2} \end{aligned} \quad (3.36)$$

by putting the boundary conditions

$$\frac{\partial \Phi}{\partial \theta} = \sigma i e^{i\Omega \tilde{\tau}} \cos \theta, \quad \frac{\partial \Phi}{\partial \sigma} = i e^{i\Omega \tilde{\tau}} \sin \theta \quad \text{at } \sigma = 1 \quad (3.37)$$

and

$$\Phi = 0 \quad \text{at} \quad \sigma = \sigma^*$$

Motivated by the boundary conditions, a solution for equation 3.36 is assumed to take the following form;

$$\Phi = e^{i\Omega \tilde{\tau}} f(\sigma) \sin \theta \quad (3.38)$$

putting equations 3.37 into 3.36 yields;

$$\left(\frac{d^2}{d\sigma^2} + \frac{1}{\sigma} \frac{d}{d\sigma} - \frac{1}{\sigma^2} - i\Omega \right) \left(\frac{d^2 f}{d\sigma^2} + \frac{1}{\sigma} \frac{df}{d\sigma} - \frac{1}{\sigma^2} f \right) = 0 \quad (3.39)$$

with the boundary conditions;

$$f = i \quad \text{and} \quad \frac{df}{d\sigma} = i \quad \text{at} \quad \sigma = 1, \quad \text{and} \quad f = 0 \quad \text{at} \quad \sigma = \sigma^* \quad (3.40)$$

as $\sigma^* \rightarrow \infty$ and $f \rightarrow 0$,

Hence the general solution to equation 3.39 is;

$$f = \frac{A}{\sigma} + B\sigma + C J_1(i\sigma\sqrt{i\Omega}) - D i K_1(\sigma\sqrt{i\Omega}) \quad (3.41)$$

where J_1 is the Bessel function of the first kind, and K_1 is the modified Bessel function of the second kind. The parameters B and C in equation 3.41 equals zero, because $f \rightarrow 0$ as $\sigma \rightarrow \infty$ and so the simplified equation is,

$$f = \frac{A}{\sigma} - D i K_1(\sigma\sqrt{i\Omega}) \quad (3.42)$$

by applying the boundary conditions in equations 3.40, A and D can be expressed in the following form:

$$A = i \left[1 + \frac{2K_1(\sqrt{i\Omega})}{(\sqrt{i\Omega})\sqrt{i\Omega}K_0} \right], \quad D = \frac{-2}{(\sqrt{i\Omega})\sqrt{i\Omega}K_0} \quad (3.43)$$

In order to evaluate the drag force and the added mass (β' and β), the force per unit length exerts on the fluid can be expressed as:

$$\tilde{F} = - \int_0^{2\pi} \{ (\tau_r - p) \cos \theta - \tau_{r\theta} \sin \theta \} r d\theta \Big|_{r=R} \quad (3.44)$$

where τ_{rr} and $\tau_{r\theta}$ are the shear stresses in the radial and the normal plane which can be obtained from:

$$\tau_{rr} = 2\eta \frac{\partial V_r}{\partial r}, \quad \tau_{r\theta} = \eta \left[r \frac{\partial}{\partial r} \left(\frac{V_\theta}{r} \right) + \frac{1}{r} \frac{\partial V_r}{\partial \theta} \right] \quad (3.45)$$

Then the solution to equation 3.44 can be written as:

$$\tilde{F} = \eta \omega \varepsilon \pi R \Omega e^{i\omega t} (1 + 2iA) \quad (3.46)$$

which can also be expressed as:

$$\tilde{F} = \rho \pi R^2 \left(-\omega^2 R \varepsilon e^{i\omega t} \beta + i\omega R \varepsilon e^{i\omega t} \beta' \right) \quad (3.47)$$

with the terms $(-\omega^2 R \varepsilon e^{i\omega t})$ and $(i\omega R \varepsilon e^{i\omega t})$ in equation 3.47 denote the acceleration or deceleration, and velocity of the fluid motion respectively.

Therefore, the term m_f and d_f required by the equation of the wire mechanics can be obtained from

$$m_f = \rho \pi R^2 \beta, \quad d_f = \rho \pi \omega R^2 \beta' \quad (3.48)$$

and finally, the parameters β and β' can be obtained in the following way

$$\beta = -1 + 2\Im(A), \quad \beta' = 2\Re(A) \quad (3.49)$$

where $\Im(A)$ and $\Re(A)$ correspond to the imaginary and real parts of A respectively.

The complete working equations used to determine both density and viscosity from the induced voltage signal are discussed in the next section.

3.5 The working equations

The working equations of the vibrating wire equipment generally are those describing the characteristics motion of the wire performing transverse oscillation. The wire is positioned vertically between two magnetic poles and electric current is passed through it which induces an emf across the wire according to the Faraday's law of electromagnetic induction. The wire in this condition would automatically begin to oscillate in transverse manner about its axes. The width of oscillation of the wire depends on two parameters mainly: (i) the viscosity of the medium in which the wire is placed and also the amount of electric current passes through the wire. An analysis of the signal measured by a lock-in amplifier revealed that the induced voltage V , measured is a sum contribution of two major components, i.e.

$$V = V_1 + V_2 \quad (3.50)$$

where V_1 is a voltage due to the electrical impedance of a stationary wire which can be expressed empirically by a complex function as follows:

$$V_1 = a + ib + icf \quad (3.51)$$

where a , b and c are adjustable parameters determined by regression and f is the frequency of vibration of the wire.

The second component V_2 is related to the velocity, v of the wire and the magnetic field strength B according to the Faraday's law of electromagnetic induction as follows:

$$V_2 \approx \frac{2}{L} \int_0^L (Bvdz) \quad (3.52)$$

and the velocity of the wire is given by the following expression;

$$v = \frac{fF_B i}{\pi^2 R^2 \rho_s [f_0^2 - f^2(1 + \beta) + f^2 i(2\Delta_0 + \beta')]} \quad (3.53)$$

$F_B \approx BI$ is the magnetic force per unit length of the wire

By substituting equation 3.53 in 3.52 and integrating along the full length of the wire, V_2 can be expressed as:

$$V_2 = \frac{2ILB^2 f_1}{\pi^3 R^2 \rho_s [f_0^2 - f^2(1 + \beta) + f^2 i(2\Delta_0 + \beta')]} \quad (3.54)$$

substituting for the amplitude given by;

$$\Lambda = \left(\frac{2ILB^2}{\pi^3 \rho_s R} \right) \quad (3.55)$$

equation 3.54 reduces to

$$V_2 = \frac{\Lambda f_1}{f_0^2 - f^2(1 + \beta) + f^2 i(2\Delta_0 + \beta')} \quad (3.56)$$

Substituting equations 3.51 and 3.56 for V_1 and V_2 in equation 3.50 provides the complete working equation of the device shown in equation 3.57

$$V = \frac{i\Lambda f}{f_0^2 - f^2(1 + \beta) + if^2(\beta' + 2\Delta_0)} + a + ib + icf \quad (3.57)$$

where V is the (complex) e.m.f. generated across the wire, Λ is an amplitude, a , b and c represent background contributions, Δ_0 is the logarithmic decrement of the wire in vacuum, f is the driving frequency and f_0 is the hypothetical resonance frequency for the case in which the wire is in vacuum and the sinker is immersed in the fluid as described in a physical model by Ciotta *et al.*[12] by:

$$f_0 = \frac{1}{2L} \left[A \sqrt{\frac{(m - \rho V)g}{\rho_w \pi R^2}} + \sqrt{\frac{ER^2}{\rho_w L^2}} + \left(1 + \frac{\pi^2}{8} \right) \sqrt{\frac{E^2 \pi R^6}{(m - \rho V)g \rho_w L^4}} \right] \quad (3.58)$$

where m and V are the mass and volume of the buoyant mass, ρ_w , R , L and E are respectively the density, radius, length and the Young's modulus of the wire material, A is an empirical parameter in the model and g is the gravitational acceleration. In equation 3.57, both β and β' are real damping quantities and are related to the densities of both the wire and the fluid according to the following dimensionless expressions:

$$\beta = k \frac{\rho}{\rho_s}, \quad \text{and} \quad \beta' = k' \frac{\rho}{\rho_s} \quad (3.59)$$

where ρ is the density of the fluid surrounding the wire k and k' are kelvin functions of Ω which in turn is a function of viscosity as:

$$\Omega = \frac{2\pi f \rho R^2}{\eta} \quad (3.60)$$

3.6 Vibrating-wire viscometer designs

Over the recent years, research in the field of vibrating-wire viscometry has received unprecedented attention. In this regards, different configurations and ways of clamping the vibrating-wire have been discovered. The two common ways of clamping the vibrating-wire are; i) clamping the wire from one fixed end and a suspended buoyant mass (BM) at the other and, ii) placing the wire between two clamped (2C) ends at constant tensioning force^[13]. Some of these configurations offer some advantages over the other depending on the situation. For instance, the (BM) can be used for simultaneous viscosity and density measurements whereas as the (2C) is often used when only viscosity measurement is required.

For all the different configurations highlighted above, tungsten wire due to its high Young's modulus and tensile strength is normally used. However, some literatures ^[14-18] have shown that materials such as stainless steel, NbZr alloy, Pt-Ir alloy and Chromel were used in some vibrating wire viscometers.

In their quest to achieve accurate viscosity and density measurements using vibrating wire viscometer, Padua *et al.*[19, 20] in 1995 designed a vibrating wire viscometer of the type (BM) using a very low density material for the buoyant mass, and this makes it very sensitive to the buoyant effects of the surrounding fluids. Hence accurate density measurements can be achieved. They tested their equipment by measuring the viscosity and density of three fluids namely: cyclohexane, 2, 2, 4-trimethyls pentane, 1, 1, 1, 2-tetraflouroethane over some range of thermodynamic conditions and both the density and viscosity measurements demonstrated high degree of accuracy in the range of ± 0.05 % and ± 2 % respectively for density and viscosity of all the fluids considered.

Vibrating wire viscometers have many advantages over other types of viscometer. These advantages include: it has a compact and simple design; it does not require bulk

movement of the fluids; it has wide applicability for different fluids (i.e. liquids and gases), both pure components and mixtures; it generates low heats compared to other viscometers; and, above all, it was described as the most accurate viscometer for high pressure/high temperature applications.[5, 6]

For high pressure applications, Trappeniers *et al.*[21] in 1979 measured the viscosity of argon up to a pressure of 1 GPa in the temperature range between (223.15 -323.15) K using a vibrating wire device. For high pressure liquid systems, a lot of researchers have used the vibrating wire viscometers in their studies, Table 3.1 gives a summary of the previous viscosity measurement using vibrating wire viscometers along with the operating conditions wire material, estimated uncertainties and the type of viscometer used.

Table 3.1: Review of literature for the development and usage of various vibrating-wire devices for viscosity measurement.

Ref.	$\frac{P}{\text{MPa}}$	$\frac{T_{\min} - T_{\max}}{\text{K}}$	Fluid	$\frac{\eta_{\min} - \eta_{\max}}{(\text{mPa} \cdot \text{s})}$	$\frac{d}{\mu\text{m}}$	$\frac{L}{\text{mm}}$	Clamp	$10^2 U(\eta)$
[4]		2.18 to 1.1	Liquid helium	0.026	25	50	2C	5
[22]	2.5	1.8 to 3.2	Pressurised 4He	0.023 to 0.07	80	50	2C	
[21]	779	223 to 323	Argon	0.11 to 0.33	100	50	2C	
[23]		80 to 323	H ₂ O, glycol, CS ₂ , O ₂ (l), Ar(g)	0.024 to 53	100	50	2C	0.13
[24]	470	174.45	Argon	0.61	50	15	2C	2.5
[25]	200	298 to 273	Dodecane, octadecane	0.22 to 6.7	100	32	BM	2
[26]	80	303 to 323	Benzene, toluene and m-xylene	0.42 to 0.89	100	54	CTS	0.5
[27]	70	298	Hexane	0.3 to 0.53	100	54	CTS	0.5
[27]	70	303 to 323	Toluene, heptane	0.42 to 0.89	100	54	CTS	0.5
[28]	250	303 to 348	Heptane	0.2 to 2	100	56	BM	3
[29]	300	303 to 348	Heptane	0.2 to 2.3	100	56	BM	3
[30]	250	303 to 348	Decane, octane, hexane, pentane and methyl benzene	0.18 to 5.9	100	56	BM	0.5
[31]	1000	273	Methane	0.01 to 0.415	50	20	2C	
[32]	5.1	231 to 343	R32, R125 at saturation	0.06 to 0.25	7.5	140	BM	1
[33]	50	235 to 343	Liquid R134a	0.11	0,24	100	56	0.6

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[34]	3.5	243 to 393	1,1-difluoroethane (R152a)	0.012 to 0.34	50	15	2C	2.8
[35]	100	260 to 300	Carbon dioxide	0.06 to 0.24	100	56	BM	0.5
[36]	450	220 to 280	Liquid CO ₂	0.5	50	20	2C	0.5
[19]	100	198 to 348	2,2,4-trimethylpentane (isooctane)	0.29 to 6	100	40	BM	3
[20]	100	199 to 298	1,1,1,2-tetrafluoroethane (R134a)	0.2 to 0.8	100	40	BM	2.5
[37]	40	197 to 348	Cyclohexane, 1,1,1,2-tetrafluoroethane, 2,2,4-trimethylpentane	0.2 to 3	100	40	BM	2
[38]	25	313 to 348	Supercritical CO ₂ -saturated PEG	20	100	40	BM	4
[39]	30	210 to 370	Methyl benzene	0.3 to 2.7	100	56	BM	0.5
[15]	20	298 to 423	Propane, Argon, Krypton	0.022 to 0.04	25	90	BM	3
[40]	0.1	210 to 370	Methylbenzene	0.3 to 2.7			BM	0.5
[41]	165	240 to 455	Natural gas mixtures	0.009 to 0.02	7			1
[42]	100	298 to 383	Pentane	0.1 to 0.43	100	28	BM	2.5
[43]	10	298 to 323	Methylbenzene	0.422 to 0.6	100	40	BM	0.4
[44]	50	303 to 432	n-hexane+hexanol	0.2 to 6.7	100	28	BM	4
[45]	80	222 to 348	Methylbenzene	0.3 to 2.2	100	40	BM	3
[46]	200	298 to 273	Dodecane, octadecane	0.22-6.7	100	32	BM	2
[47]	0.1	288 to 308	Diisodecylphthalate	120	200	60	2C	1
[48]	75	298	Methane+n-decane	0.08 to 1.65	100	28	BM	3
[49]	20	213 to 298	Toluene	0.55 to 3.3	100	40	CTS	1.5
[50]	137	298 to 398	Methane+n-decane	2.52 to 0.597	150	26	2C	2
[51]	170	303 to 448	CO ₂ +squalane	22.0 to 0.41	100	70	BM	2
[52]	140	298 to 473	CO ₂ +n-hexadecane	0.453 to 0.267	150	70	BM	2
[53]	135	298 to 448	Pure hydrocarbon and their mixtures	0.33 to 16.13	150	50	2C	2

BM: Buoyant Mass at one end 2C: clamped at both ends CTS: clamped at both ends with constant tensioning system

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Modelling Approaches

4.1 Introduction

Even though experimental measurement is generally considered the primary source of viscosity data, it is practically impossible to measure the viscosity at all thermodynamic states of temperature, pressure and composition. In this regard, predictive models in the form of mathematical expressions provide the flexibility for determining viscosity of fluid samples at a wide range of thermodynamic conditions in a convenient and inexpensive manner. Several models for predicting the viscosity of pure compounds and their mixtures have been proposed in the literature. These models can be broadly grouped into: highly theoretical; semi-theoretical; and simple empirical correlations for both dilute/dense gas and liquid. Theoretical models are fundamentally based on kinetic theory and statistical mechanics in which viscosity is expressed in terms of intermolecular potential functions. These models have relevant theoretical backgrounds such as corresponding states theory, reaction rate theory, and applied statistical mechanics. On the other hand, semi-theoretical models are derived to incorporate adjustable parameters that take different values for different fluids and are determined from experimental viscosity measurement for the given fluid. Empirical models are simple correlations developed mostly based on experimental measurements and generally relate viscosity to the primary thermodynamic variables such as temperature and pressure or density. For mixtures, the viscosity is usually determined from the viscosities of the pure species by employing appropriate mixing rules. Detailed review of these models can be found elsewhere^[1-5], however, some of the relevant theories and models for dilute gas/vapour, dense gas/liquid as well as models for estimating the viscosity of mixtures will be highlighted.

4.2 The kinetic theory

Kinetic theory is a part of non-equilibrium statistical mechanics that relates macroscopic properties of an entire system to the microscopic properties of the individual molecules and their interaction potentials. For dilute gases, the theory assumes a macroscopic system at densities sufficiently low so that the molecules spend more time in free flight and interact only through binary encounters and yet, the densities are high enough to ensure that the effects of molecule-wall collisions can be neglected compared to those of molecule-molecule encounters[6].

Temperature and pressure are the two properties commonly used in specifying quantities in many engineering applications, for transport properties (e.g. viscosity) however, temperature and density (or molar volume) are the key variables. Thus, viscosity as a key

transport property of liquids can be conveniently described as a function of temperature and density as follows:

$$\eta(\rho_n, T) = \eta^0(T) + \Delta\eta(\rho_n, T) + \Delta\eta_c(\rho_n, T), \quad (4.1)$$

where, ρ_n is the molar density, T is the absolute temperature, η^0 is the dilute gas viscosity, $\Delta\eta$ is the excess viscosity and $\Delta\eta_c$ is the critical enhancement to viscosity

4.3 Dilute gas/vapour

The models for gas or vapour phase are generally based on the kinetic theory of gases, and a detailed review of these models have been described by Monnery, *et al.*[2]. The simplest approach of these models assumed that the molecules behave as identical non-interacting hard spheres with diameter σ and mass m , moving along a free path colliding with each other with an average velocity given by[7],

$$\langle c \rangle = \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}, \quad (4.2)$$

where k is the Boltzmann's constant, T is the temperature and m is the molar mass.

If the molecules are in continuous random motion and exert no force on each other except on contact, then a simple kinetic model can be used to expressed the dilute gas viscosity as[1, 6]:

$$\eta^0 = \frac{2}{3\pi} \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \frac{1}{\sigma^2} \quad (4.3)$$

where, σ is the effective rigid sphere diameter.

However, if the molecules attract or repel each other due to intermolecular forces, the classical Chapman-Enskog^[8] (CE) theory is applied. This theory takes into account the interaction between colliding molecules and expressed the viscosity of a real dilute gas as a function of a dimensionless collision integral as follows:

$$\eta^0 = \frac{5}{16} \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \frac{f_n}{\sigma^2 \Omega^*(T^*)} \quad (4.4)$$

here, $\Omega^*(T^*)$ is the dimensionless collision integral which for hard sphere molecules is equal to unity[1], otherwise is related to the intermolecular potential of the species and f_n is the higher order correction factor, usually set to unity for the initial approximation.

The dilute gas viscosity equation given by equation 4.3 above is clearly independent of density and hence described as the viscosity at zero density denoted as η^0 , and in practice this can only be true at $\eta = \eta^0$.

4.4 Moderately dense fluid

Enskog[9] proposed an equation which describe the viscosity coefficient of a dense hard-sphere gas. The equation is an empirical modification of Boltzman's theory which accommodates the finite size of molecules. Enskog's equation relates the three transport properties (i.e. viscosity, diffusivity and thermal conductivity) for a dense gas denoted by subscript E to its corresponding value in dilute gas region denoted by superscript 0 . For viscosity, the Enskog equation can be written as follows.

$$\frac{\eta_E}{\eta^0} = \left[\frac{1}{\chi(\sigma)} + \frac{0.8b}{V_m} + 0.761\chi(\sigma) \left(\frac{b}{V_m} \right)^2 \right] \quad (4.5)$$

here η_E is the viscosity value determined via Enskog equation, η^0 is strictly the hard sphere dilute gas viscosity given by equation 4.4 when $f = 1.0160$ and $\Omega^* = 1$, and b is the Van der Waal's co-volume factor defined by:

$$b = B + T \left(\frac{\partial B}{\partial T} \right) = 2\pi \frac{N_A \sigma^3}{3}. \quad (4.6)$$

In equation (4.5), σ is the radial distribution function at contact, which is unity at low pressure, and can generally be obtained from the following:

$$p_t = T \left(\frac{\partial p}{\partial T} \right)_p = RT \frac{1}{V_m} \left[1 + b \frac{\chi(\sigma)}{V_m} \right], \quad (4.7)$$

where p_t is the thermal pressure. N_A is Avogadro's constant, R is the universal gas constant and B is the second viral coefficient. When equations 4.6 and 4.7 are applied together with equation 4.5 the scheme is known as the modified Enskog theory.

4.5 Dense fluid

Unlike the dilute gas situation, in dense fluids momentum transfer is predominantly by collision. As the density increases, the rate of collision between the neighbouring molecules also increases rapidly, mainly because the distance between the molecules has significantly been reduced by their finite volume. In this regards, it is important to note that in deriving his equation, Enskog makes two principal assumptions: that the molecules are made-up of hard sphere and there are no correlated collisions between the molecules. But in practice both assumptions cannot be applied to a dense fluid as the molecules collide in a correlated manner as the density increases, and also the molecular

shape cannot be described as a hard sphere. Therefore there is a need for a clear understanding of the shape of the molecules as well as the interaction flexibilities in the higher density region. This can be achieved with the aid of some advances in the use of computer technology such as molecular simulations.

4.5.1 Molecular dynamic simulations

Improvements in computational power which enables more and longer simulation runs have led to significant success in predicting transport properties of very complex systems. In molecular simulation, the technique utilizes the Gibb's assumption which relates macroscopic properties of an infinite system to the time average. In this approach, each molecule is assigned an initial position and velocity and then, the forces calculated through intermolecular potential functions[10]. The classical Newtonian equations of motion are integrated to determine the particle location and velocity in a given period time, t . Subsequently, the statistical mechanics function relates both macroscopic and microscopic properties of the system. Molecular dynamic simulation can be performed in many ways depending on the intended application. For instance, when set of transport coefficients at a particular operating condition per run are required, the simulation is done in an equilibrium condition, whereas simulating at non-equilibrium conditions only provides one single property per run. Molecular simulation is also employed to determine the effect of correlated molecular collisions on the transport properties of a hard-sphere fluid[11].

4.5.2 Friction Theory

The friction theory is a mechanical approach for modelling the viscosity of fluid substances. In this approach, viscosity of dense fluids is described by two terms namely; the dilute gas terms and friction term given by[12]:

$$\eta = \eta_0 + \eta_f \quad (4.8)$$

where, η_0 is the dilute gas viscosity term and η_f is the friction term.

The gas term is given as per equation 4.4 whereas, the friction term can be obtained by relating the viscosity to the Vander Waals attractive and repulsive pressure terms via the Amontons-Coulombs friction law as[12]:

$$\eta_f = k_r p_r + k_a p_a \quad (4.9)$$

where, k_a and k_r are defined by the ratios between the Amontons-Coulomb coefficients of kinetic friction and the rate of shear du/dh and the pressure terms p_r and p_a are the Vander Waals repulsive and attractive pressure terms respectively.

Friction theory has been used to predict the viscosities of different n-alkanes and there mixtures in the past. An example of high-pressure, high-temperature application of this theory can be found in Burgess *et al.*[13]

4.5.3 Free volume theory

In a similar approach as the friction theory, the free volume theory express the total viscosity of fluid substance as a sum of two terms as:

$$\eta = \eta_0 + \eta_{fv} \quad (4.10)$$

again, the first term represent the dilute gas viscosity giving in equation 4.4 and the second term is the free-volume term.

Doolittle^[14] proposed that the free-volume term is an exponential function of the reciprocal of the fraction of the space within a system that is not occupied by molecules (i.e. free-volume of the system f_v) given as[13]:

$$\eta_{fv} = A e^{B/f_v} \quad (4.11)$$

Subsequently, Allal *et al.*[15] proposed that the free-volume of the system f_v is dependent on the ratio PM/ρ , the energy required to create vacant vacuums required for diffusion, and a barrier energy, $\alpha\rho$ which a molecule must overcome to be able to diffuse. The general form of equation 4.12 is as follows[13]:

$$\eta_{fv} = \frac{\rho L \left(\alpha\rho + \frac{PM}{\rho} \right)}{\sqrt{3RTM}} \exp \left[B \left(\frac{\alpha\rho + \frac{PM}{\rho}}{RT} \right)^{1.5} \right] \quad (4.12)$$

Equation 4.12 require only the molar mass M (kg/mol) and pressure p /MPa, temperature T /K and density ρ values and the other pure component parameters L /Å, α /(m³/mol·s²), and B (dimensionless) as inputs. Again, examples of applications of free volume in high-pressure, high-temperature systems can be found in^[13].

4.6 Mixture viscosity

The viscosity of a fluid mixture is normally obtained from the viscosity of the pure components of the mixture via a suitable mixing rules. These mixing rules are usually simple mole, mass or volume fraction averages functions of the viscosity of pure components in the mixtures. For instance, the Grunberg-Nissan[16] mixing rule can be used to obtain the viscosity of simple liquid mixtures from the viscosities of the pure components in the mixture.

For a dense fluid, the Enskog theory can be extended to calculate the viscosity of multi-components mixtures at low pressure. The theory is principally based on the kinetic

theory of the dilute gas and the results can be expressed for a mixture of N -components as:

$$\eta^0 = \frac{\begin{vmatrix} H_{11} & \cdots & H_{1N} & x_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & x_N \\ x_1 & \cdots & x_N & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix}}, \quad (4.13)$$

where,

$$H_{ii} = \frac{x_i^2}{\eta_i^0} + \sum_{k=1, k \neq i}^N \frac{2x_i x_k}{\eta_{ik}} \frac{m_i m_k}{(m_i + m_k)^2} \left(\frac{5}{3A_{ik}^*} + \frac{m_k}{m_i} \right), \quad (4.14)$$

and for $i \neq j$

$$H_{ij} = -\frac{2x_i x_j}{\eta_{ij}^0} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{5}{3A_{ij}^*} - 1 \right), \quad (4.15)$$

where by m_i and x_i denote the molecular mass and mole fraction of specie ' i ' in the mixture of N - components respectively. Also the interaction viscosity between pairs is given by:

$$\eta_{ij}^0 = \frac{5}{16} \left(\frac{m_{ij} k T}{\pi} \right)^{\frac{1}{2}} \frac{1}{\sigma_{ij}^2 \Omega_{ij}^{(2.2)*}}, \quad (4.16)$$

with the parameters m_{ij} and σ_{ij} are respectively defined as

$$m_{ij} = 2 \frac{m_i m_j}{m_i + m_j} \quad \text{and} \quad \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j). \quad (4.17)$$

Here the parameters $\Omega^{(2.2)*}$ and A_{ij}^* are related to the potential energy function of the pair-wise interaction, and both can be related to the principle of corresponding states with Argon as a reference potential. Again, for monatomic gases, they can be approximated as a universal function of reduced temperature given by[17]:

for $1 < T^* < 90$,

$$\ln(\Omega_{2.2}) \equiv \ln \left(\frac{(\Omega^{(2.2)*})}{f_n} \right) = \sum_{i=0}^4 a_i (\ln T^*)^i \quad (4.18)$$

and for $1 < T < 25$

$$\ln(A_{ij}^*) \equiv \ln \left(\frac{\Omega^{(2.2)*}}{\Omega^{(1.1)*}} \right) = \sum_{i=0}^4 b_i \ln(T^*)^i \quad (4.19)$$

and the reduced temperature described in terms of molecular potential ε_{ij} is follows.

$$T^* = \frac{kT}{\varepsilon_{ij}} \quad (4.20)$$

To determine the dilute gas viscosity, the coefficients a_i and b_i in equations 4.18 and 4.19 must be obtained by fitting the well depth ε and the molecular diameter σ from experimental measurements. Chung *et al.*[18] proposed that for a pure components, the two coefficients can be obtained from measurement of macroscopic properties as shown in the equation below.

$$\varepsilon = \frac{T_c k}{1.2593} \quad \text{and} \quad \sigma = 0.809 V_c^{1/3} \quad (4.21)$$

Equation 4.21 can be corrected by multiplying with F_C to accommodate the molecular shapes and polarities, where F_C is the correction factor given by:

$$F_C \equiv 1 - 0.2756\omega + 0.059035\mu_r^4 + k \quad (4.22)$$

where, ω is the acentric factor, μ_r is the dipole moment, and k is the polarity correction factor

Similarly, the Chapman-Enskog theory can be applied in a semi-theoretical approach to extend its application to the dilute gas viscosity of a mixture. A number of approaches are described in the literature[19, 20]. Example of these approaches includes, the Wilkes's[21] method which is relatively simple and derived from kinetic theory of gases. This theory expressed dilute gas viscosity of a mixture as a function of the dilute gas viscosity of the pure species as follows.

$$\eta_{\text{mix}}^0 = \frac{\sum_{i=1}^n x_i \eta_i^0}{\sum_{i=1}^n x_i \phi_{ij}} \quad (4.23)$$

where,

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\eta_i^0}{\eta_j^0} \right) \left(\frac{m_j}{m_i} \right)^{0.25} \right]}{4 \left(1 + \frac{m_j}{m_i} \right)^{0.5}} \quad (4.24)$$

Furthermore, Hering and Zipperer[22] proposed an even simpler relation for evaluation of parameter ϕ_{ij} as follows.

$$\phi_{ij} = \left(\frac{m_j}{m_i} \right)^{0.5} \quad (4.25)$$

Even though equations 4.24 and 4.25 differ considerably in complexity, but yet, they provide very close estimation of the parameter ϕ_{ij} , relative to the experimental viscosity data.

For highly asymmetric mixtures however, simple mixing rules usually provide unsatisfactory results due to the extremely-high viscosity ratio of the individual components in the mixture. On this basis, we aimed to test the predictive performance of two promising models namely: the VW model and the extended hard sphere model in conjunction with different mixing rules against the experimental data. This would serve as a follow-up from the previous studies on exploring the potentials of these promising theoretical models in predicting the viscosity of asymmetric mixtures by Ciotta *et al.*[11, 23] in our group. The subsequent sections highlight the theoretical backgrounds of these models.

4.6.1 Hard sphere (HS) theory

The theory of hard sphere provides a basis for successful correlations of transport properties of dense fluids. One of the advantages of this theory is that it can be used for a very wide range of densities starting from dilute gas region to dense fluids and ultimately to solidification[24]. In addition, the theory reasonably conforms to the popular Van der Waals theory in which the molecules can be assumed to have a hard core repulsive interactions and a long range attractive energy. In this respect, the molecules are assumed to move in a straight path between elastic collision from adjacent molecules.

In order to use this theory, it is necessary to assign a value to the core/hard sphere diameter. In a real fluid, the molecules collide with each other at shorter diameters at higher temperatures and consequently, the core diameter is assumed to be temperature dependent. The inherent complexity and the uncertainties involved in evaluating the core/hard sphere diameter led Dymond and Assael[25] to introduced the following dimensionless quantity η^* called the reduced viscosity defined by:

$$\eta^* = \left(\frac{\eta}{\eta^0} \right) \left(\frac{V_m}{V_0} \right)^{2/3} \quad (4.26)$$

where, V_m is the molar volume and V_0 is the molar volume at close packing of the spherical molecules, which is given for hard sphere by:

$$V_0 = \frac{N\sigma^3}{\sqrt{2}} \quad (4.27)$$

Substituting the dilute gas viscosity equation 4.4, the close pack volume equation 4.27 into equation 4.26 above yields:

$$\eta^* = \frac{16}{5} (2N_A)^{1/3} \left(\frac{\pi}{MRT} \right)^{1/2} (V^*)^{2/3} \eta \quad (4.28)$$

In equation 4.28 above, the ratio V_m/V_0 is replaced by a dimensionless term V^* called reduced volume.

Equation 4.28 permits the calculation of viscosity without knowing the core diameter σ . Also a close observation reveals that the equation is only a function of the dimensionless volume V^* . Several studies by Dymond [25-30] and others established a universal curve for viscosity as a function of molar volume defined by the following equation.

$$\log \eta^* = \sum_{i=0}^7 a_{\eta,i} \left(\frac{V_m}{V_0} \right)^{-i} \quad (4.29)$$

Here, a_i ($i = 0$ to 7) are the coefficients of the reduced volume given in Table 4.1 and are determined experimentally. It was also described that the characteristic core volume of the spheres V_0 is a weak function of temperature as expressed as:

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = \sum_{i=0}^N g_i (T / \text{K})^i \quad (4.30)$$

where g_i are the weak temperature-dependent coefficients.

Chandler *et al.*[31] and Dymond *et al.*[28] proposed a shape correction factor also called roughness factor R_η to account for non-sphericity of the molecules. For monoatomic fluids the roughness factor is considered to be unity. Whereas for polyatomic fluids and long chain hydrocarbons, Assael *et al.*[32] determined the values of V_0 and R_η for n-alkanes from methane to n-hexadecane through curve fitting of an extensive experimental viscosity data using equations 4.30 and 4.31 respectively.

$$R_\eta = 0.995 - 0.0008944 C_n + 0.005427 C_n^2, \quad (4.31)$$

and the general equation for correlating viscosity becomes:

$$\eta^* = \frac{16}{5} (2N_A)^{1/3} \left(\frac{\pi}{MRT} \right)^{1/2} \frac{\eta V_m^{2/3}}{R_\eta} \quad (4.32)$$

Viscosities of different members of n-alkanes were estimated using the generalised values for R_η and V_0 and, in all cases the generalised equation 4.32 gives consistent prediction with average absolute relative deviation of not more than 2.8 %.

4.6.2 The extended hard sphere scheme

The extended hard-sphere scheme developed by Ciotta *et al.*[23] is an extension of the original hard-sphere model developed by Dymond and Assael[26, 30, 32-36] and their collaborators. The scheme was developed to address the following key limitations of the original hard sphere model[23].

- The original hard sphere model is not able to reproduce the experimental data in both the dilute gas region (i.e. $V_m/V_0 > 5$) and very dense fluid region (i.e. $V_m/V_0 < 1.5$)[23]
- The original hard sphere model is very sensitive to density, especially in the high density region where 1 % deviation in density could lead up to 15 % deviation in viscosity.

The extended hard sphere scheme behaves correctly in the limit of low densities while at the same time offering improved prediction accuracy at high-density regions[23]. The new scheme used experimental data on several hydrocarbons and successfully extends the range of validity of the original hard sphere model to $(1.2 \leq V_m/V_0 \leq 5)$. The expression of the extended hard sphere scheme is given as:

$$\Delta\eta^* = \frac{16}{5}(2N_A)^{\frac{1}{3}} \left(\frac{\pi}{MRT} \right)^{\frac{1}{2}} V_m^{\frac{2}{3}} \frac{\eta - \eta^0}{R_\eta} \quad (4.33)$$

where, $\Delta\eta^*$ is the excess viscosity and like in the original hard sphere model, it is related to the characteristic core volume V_0 via the expression for the universal curve as shown below.

$$\log_{10}(\Delta\eta^* + 1) = \sum_{i=0}^7 b_{\eta,i} \left(\frac{V_m}{V_0} \right)^{-i} \quad (4.34)$$

In order to implement the extended scheme, the expressions for both V_0 and R_η from the original hard sphere model were retained and the coefficients of equation 4.34 are given in

Table 4.1: Coefficients of universal curves of Hard Sphere and the Extended Hard Sphere

i	$a_{\eta,i}$	$b_{\eta,i}$	$^*c_{\eta,i}$
0	1.09450	0.00000	0.00000
1	-9.26324	6.27593	5.14262
2	71.03850	-48.53426	-35.5878
3	-301.90120	243.27241	192.05015
4	797.69000	-652.14967	-573.37246

5	-1221.97700	972.83819	957.41955
6	987.55740	-763.26018	-833.36825
7	-319.46360	251.45411	299.40932

*Coefficients of the Extended Hard Sphere model used by Mylona *et al.*[37] in chapter seven

4.6.3 The Hard sphere model for mixtures

Assael *et al.*^[35] extended the application of hard sphere model to mixtures of n-alkanes and other mixtures of similar molecules. This was achieved by applying a mole fraction linear mixing rule with the assumption that there is no change in volume during mixing and the corresponding fluids behaves like a single component liquid[6]. The parameters $V_{0,m}$ and $R_{\eta,m}$ for the mixture were approximated from the average values of the individual species in the mixture as:

$$V_{0,m} = \sum_{i=1}^n x_i V_{0,i}, \quad R_{\eta,m} = \sum_{i=1}^n x_i R_{\eta,i} \quad \text{and} \quad M_m = \sum_{i=1}^n x_i M_i \quad (4.35)$$

where, x_i and M_i are the mole fraction and molar mass of the pure components and $V_{0,i}$, $R_{\eta,i}$ and ρ_i are the closed packing volume, roughness factor and molar mass of the individual components in the mixture respectively. $V_{0,m}$, $R_{\eta,m}$ and M_m are properties of the mixture.

This approach has been tested in this work for n-alkanes binary, ternary and quaternary mixtures, and the model agrees reasonably well with some experimental data. For example, for the binary mixture of *n*-hexane + *n*-hexadecane at ambient conditions studied by Aucejo *et al.*[38], significantly smaller deviations in terms of $\Delta_{AAD,\eta}$ of 0.9 % and $\Delta_{MAD,\eta}$ of 1.8 % were estimated. However, it was found that as the pressure increases, higher deviations were recorded due to the uncertainty in density at higher pressures. Similarly, it was observed that as the molar mass ratio of the components becomes great and the molecules differ much in size and/or shape, the deviation increases significantly. For instance the estimated deviations of CO₂ + *n*-hexadecane from Ciotta's[11] study were as high as $\Delta_{AAD,\eta}$ of 12.9 % and $\Delta_{MAD,\eta}$ of up to 44.8 %.

The same procedure as that of the original hard sphere model is followed in applying the extended hard sphere scheme to mixtures.

4.6.4 The Vesovic-Wakeham scheme

This model has its theoretical basis from the rigid sphere theory[6] of dense fluids. The theory is modified in a self-consistent manner to account for the behaviour of real gases.

Di pippo *et al.*[39] proposed a correlation for estimating the viscosity of a dense gas mixture containing N rigid sphere components as described by[40]:

$$\eta = -\eta^0 + \kappa_{\text{mix}} \quad (4.36)$$

where, the dilute gas viscosity term η^0 was defined in equation 4.13 and the individual elements in equations 4.14 and 4.15.

and the parameter κ_{mix} is defined as;

$$\kappa_{\text{mix}} = \frac{3}{\pi} \rho^2 \sum_{i=1}^N \sum_{j=1}^N x_i x_j \chi_{ij} \alpha_{ij}^2 \eta_{ij}^0 \quad (4.37)$$

where ρ is the molar density, m_j and x_j are the mass and mole fractions of component j respectively. The parameters η_i^0 and η_j^0 are the dilute gas viscosities for species i and j and, η_{ij}^0 is the interaction viscosity of an i - j pair. The quantity α_{ij} is referred to as the free path shortening for an i - j collision in a dense fluid and, χ_{ij} is the radial distribution at contact for species i and j in the mixture.

The free shortening parameter α_{ij} is related to the cube of the core diameter σ_{ij} and Avogadro's constant N_A in the original Thorne-Enskog theory as shown below:

$$\alpha_{ij} = \frac{8\pi N_A \sigma_{ij}^3}{15} \quad (4.41)$$

where, $\sigma_{ij} \equiv \frac{(\sigma_{ii} + \sigma_{jj})}{2}$, and σ_{ii} is the core diameter of component i in the mixture which is equal to core diameter of the pure component i , σ_i

The radial distribution function χ_{ij} can be related to the core diameter of the components in many ways. The Lebowitz's solution of the Percus-Yevick[41] equation express χ_{ij} as a function of all the three core diameters as shown below:

$$\chi_{ij} = \frac{1}{1 - \zeta_3} + \frac{3\sigma_{ii}\sigma_{jj}\zeta_2}{2\sigma_{ij}(1 - \zeta_3)^2} \quad (4.42)$$

where,

$$\zeta_1 = \left(\frac{\pi \rho N_A}{6} \right) \sum_{k=1}^N x_k \sigma_{kk}^3 \quad (4.43)$$

Thus, knowing the dilute gas viscosities of the pure components and core diameters σ_{ii} , σ_{jj} and σ_{ij} should be enough to compute the viscosity of any mixture using this model. On the other hand, it was observed that viscosity of mixtures calculated using the original Thorne-Enskog theory are often higher than the experimental viscosities, this however is

attributed to the failure of the theory to include the effects of correlated motion and underestimation of intermolecular forces[42].

The Vesovic-Wakeham (VW) model effectively overcomes the limitations of Thorne-Enskog theory by using a pseudo-mean free path shortening parameter $\bar{\alpha}_{ij}$ and a pseudo radial distribution function $\bar{\chi}_{ij}$ in place of the original parameters α_{ij} and χ_{ij} . The pseudo-parameters are determined from the viscosity of the pure components as follows:

$$\bar{\chi}_i(\rho, T) = \frac{\beta (\eta_i - \rho \bar{\alpha}_i \eta_i^0)}{2 \rho^2 \bar{\alpha}_i^2 \eta_i^0} \pm \beta \left[\left(\frac{\eta_i - \rho \bar{\alpha}_i \eta_i^0}{2 \rho^2 \bar{\alpha}_i^2 \eta_i^0} \right)^2 - \frac{1}{\beta \rho^2 \bar{\alpha}_i^2} \right]^{1/2} \quad (4.44)$$

where, $\beta = 0.8299$

solving equation 4.44 produces two possible roots (i.e. a positive $\bar{\chi}_i^+$ and a negative $\bar{\chi}_i^-$ root) and, the ideal solution is obtained at a particular molar density ρ (called switched-over density) at which the two roots are equal. The switched-over density can be obtained from the solution of the equation[42]

$$\left. \frac{\partial \eta_i}{\partial \rho} \right|_T = \frac{\eta_i}{\rho} . \quad (4.45)$$

The application of VW model in predicting viscosity of mixture of various components involved replacing the original mixture radial distribution function χ_{ij} determined from the Lebowitz's solution of Percus-Yevic's equation 4.42 with a pseudo-radial distribution function for the mixture $\bar{\chi}_{ij}$ determined from the contribution of $\bar{\chi}$ of each component using appropriate mixing rule. In the original VW model, the mixing rule used for the pseudo-radial distribution function of the mixture takes the following form[42]:

$$\bar{\chi}_{ij} = 1 + \frac{2}{5} \sum_{k=1}^N x_k (\bar{\chi}_k - 1) + \frac{\frac{6}{5} (\bar{\chi}_i - 1)^{1/3} (\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^N x_k (\bar{\chi}_k - 1)^{2/3}}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \quad (4.46)$$

The VW method described above is an illustration of the early development of the method for mixtures containing similar molecules and molecular mass, thereby allowing for representation of each molecule by an effective hard-sphere. However, if the molecules are different in size and shape as in the case of asymmetric mixtures, a chain representation of the molecules produces more accurate results compared to the hard-sphere representation. de Wijn *et al.*[43] successfully extended the VW method to liquid mixtures containing chain-like molecules using an Enskog-like analysis described in section 4.5. This approach treated the molecules of the mixture as tangentially bonded

chains of equally-sized hard spherical segments^[43] and so, the parameters in equations (4.36 to 4.40) of the original VW method are replaced by the properties of the segments and the detailed description of this approach can be found in de Wijn *et al.*[43].

The VW-chain model has been tested in this work on a number of fluid mixtures ranging from binary to ternary mixtures of hydrocarbon components at a wide range of temperature and pressure. It was found that the model proved successful for certain type of mixture of fluids as demonstrated in Table 4.2 in section 4.9.1. For instance, for the binary mixtures of *n*-octane + *n*-dodecane studied by Caudwell[10], it was observed that the model presents an $\Delta_{AAD,\eta}$ of about 1 % and $\Delta_{MAD,\eta}$ of only 5 %. This low deviation is attributed to the fact that the molecules of the two components of the mixture are similar in nature and the degree of asymmetry (molar mass ratio of the components) is also low about 1.5. However, when a third component (propane) entirely different from the other two was added, the $\Delta_{AAD,\eta}$ rose to about 3%. Similarly, the $\Delta_{MAD,\eta}$ also increases tremendously to about 17%. Consequently, it is possible to conclude that, the deviations of VW model increases with increase in molar density as well as the asymmetric index of the mixture.

4.7 Assessment of performance of VW and HS models in predicting the viscosity of asymmetric mixtures

Although a large body of viscosity data can be found in the literature for simple liquid hydrocarbon mixtures, such data for asymmetric mixtures are very limited especially for the highly asymmetric mixtures involving higher-molecular mass hydrocarbons (e.g. *n*-hexadecane, squalane and higher members). For instance, to the author's knowledge there is no single published study on the viscosity of mixtures of either *n*-hexadecane or squalane with dissolved methane. This kind of mixtures can be of interest to researchers because it could be used to serve as a model for crude oil with dissolved gases. In the following section, some relevant available data found in the literature were critically analysed and tested against the predictions of the Dymond-Assael hard-sphere model implemented for each system in this work and Vesovic-Wakeham[43] calculated using an in-house codes obtained in a private communication from Riesco[44].

The analysis began by examining the performance of the models on some simple hydrocarbon liquid mixtures at ambient conditions, and continued with asymmetric mixtures at a wide range of temperature and pressure. Finally, the analysis was concluded by examining the performance of these models on highly asymmetric mixtures containing a dissolved non-hydrocarbon supercritical component. In all, a total of 1567 data points for five different mixtures were examined. For each data point, a corresponding viscosity value was computed using the two models and the deviations

relative to the reported experimental observations were described and finally some conclusions were drawn.

4.7.1 Simple liquid hydrocarbon mixtures at ambient conditions

Aucejo *et al.*[45] reported the viscosity, density and refractive index of 36 n-alkane binary liquid mixtures measured using an Ubbelohde viscometer and an Anton Paar precision densimeter for kinematic viscosity and density measurements respectively. The measurements were conducted at ambient pressure $p = 0.101$ MPa, temperature $T = 298.15$ K and in full composition range ($0 \leq x_1 \leq 1$). Among the systems studied, the binary mixtures of *n*-hexane + *n*-hexadecane is particularly of interest to the present study because of the high molar mass ratio of the constituents of the mixture. The reported experimental data for these mixtures were critically analysed against the predictions of the two models (the HS and VW models), and the relative deviations of the predicted values from the reported experimental observations were calculated.

The relative deviations were plotted against pressure for both models and the results were shown in Figures 4.1(a) and (b) below.

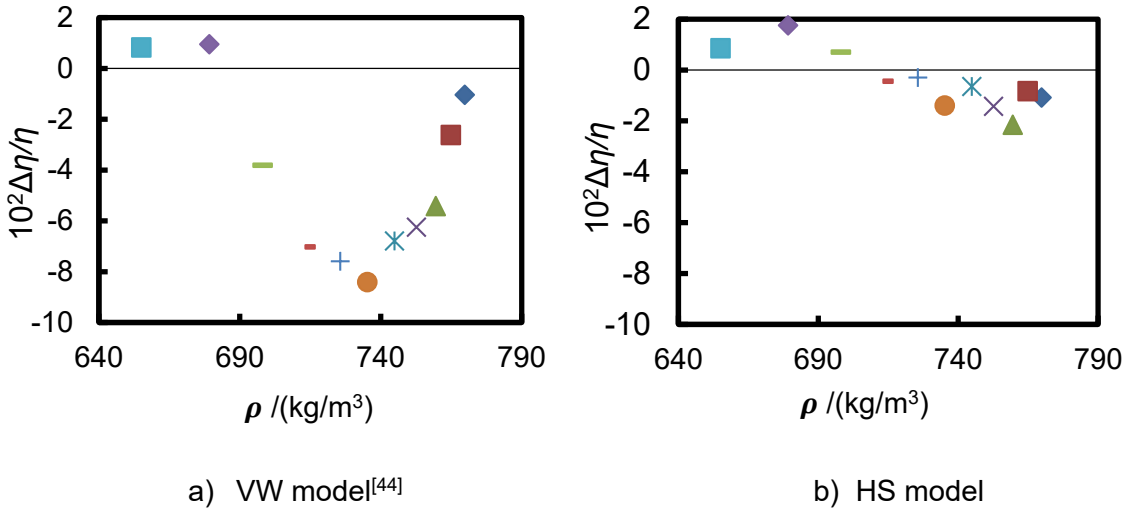


Figure 4.1: Relative deviations of VW and HS models from Aucejo[45]'s results at $T / K = 298.15$ and $p / \text{MPa} = 0.101$: $\times$, $x_1 = 0.3$; $\blacklozenge$, $x_1 = 0$; $\blacksquare$, $x_1 = 0.103382$; $\blacktriangle$, $x_1 = 0.1966$ and $\ast$, $x_1 = 0.4037$; $\bullet$, $x_1 = 0.5142$; $+$, $x_1 = 0.6072$; $-$, $x_1 = 0.7062$; $-$, $x_1 = 0.8048$; $\blacklozenge$, $x_1 = 0.9026$ and $\blacksquare$, $x_1 = 1$

Furthermore, agreement of the overall datasets with the two models were described in terms of the percentage average absolute relative deviation $\Delta_{\text{AAD},\eta}$, maximum absolute deviation $\Delta_{\text{MAD},\eta}$ and average bias $\Delta_{\text{Bias},\eta}$ given by:.

$$\Delta_{\text{AAD},\eta} = \frac{1}{N} \sum_{i=1}^N \left(\left| \frac{\eta_{\text{Exp.}} - \eta_{\text{Cal.}}}{\eta_{\text{Cal.}}} \right| \right), \quad (4.47)$$

$$\Delta_{\text{MAD},\eta} = \text{Max} \left(\frac{|\eta_{\text{Exp.}} - \eta_{\text{Cal.}}|}{\eta_{\text{Cal.}}} \right), \quad (4.48)$$

and

$$\Delta_{\text{Bias},\eta} = \frac{1}{N} \sum_{i=1}^N \left(\frac{\eta_{\text{Exp.}} - \eta_{\text{Cal.}}}{\eta_{\text{Cal.}}} \right). \quad (4.49)$$

From Figures 4.1(a) and (b) above, it can be seen that the relative deviations of the VW model were distributed between - 8 % and +1 %, with an $\Delta_{\text{AAD},\eta}$ of 3 % and a strong negative bias of -4 %. In contrast, the relative deviations of the hard sphere model were narrowly distributed in the range of -2 % to + 2 %, with an $\Delta_{\text{AAD},\eta}$ of 1 % and weak negative bias of -1 %. It follows from the figures that, both models over-predicted the experimental observations. However, the deviations of the VW model were more than four times those of the hard sphere model.

4.7.2 Asymmetric hydrocarbon liquid mixtures over wide range of temperatures and pressures:

Caudwell^[10] conducted an experimental viscosity measurements on binary liquid mixtures of *n*-octane + *n*-dodecane using a vibrating wire viscometer. Measurements were conducted on about 228 data points in the temperature range ($298.15 \leq T / \text{K} \leq 473.15$) and pressures up to $p / \text{MPa} \leq 200$ in the full compositions range $0 \leq x_1 \leq 1$.

The experimental results were compared with the results obtained from the predictions of the two theoretical models and the relative deviations of the predicted values were computed as shown in the Figures 4.2(a) and (b).

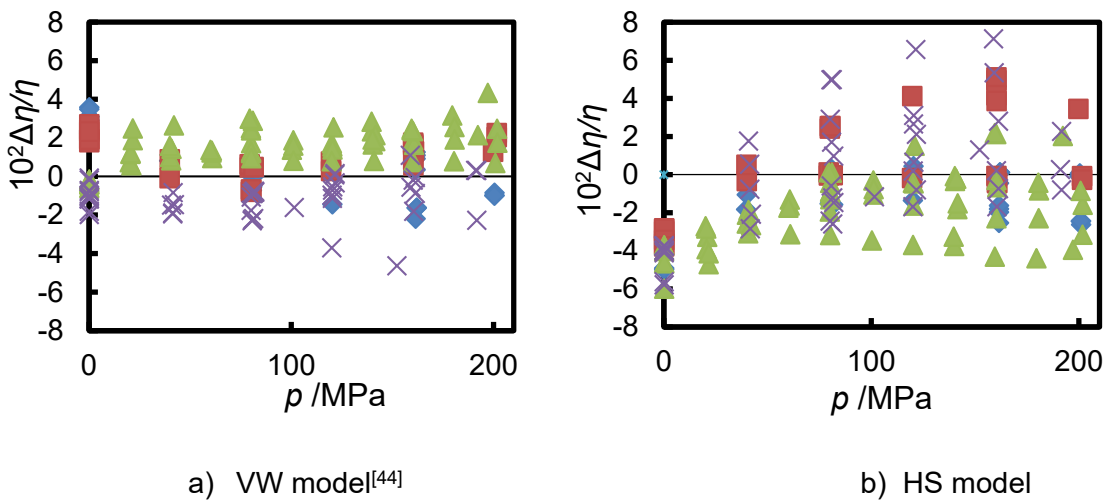


Figure 4.2: Relative deviations of VW and HS models from Caudwell[46]'s results (binary) in the temperature range $298.15 \leq T / \text{K} \leq 400.00$ and pressures, $p / \text{MPa} \leq 200$. $\times$, $x_1 = 0$; $\blacklozenge$, $x_1 = 0.743$; $\blacksquare$, $x_1 = 0.434$ and $\blacktriangle$, $x_1 = 1$

From the figures above, it can be seen that the relative deviations of the VW model were distributed between -4.6 % and +4.34 % with an $\Delta_{AAD,\eta}$ of 1.3 % and a positive bias of 0.6 %. On the other hand, the relative deviations of the hard sphere model were spread in the range -6.0 % to 7.1 % with an average $\Delta_{AAD,\eta}$ of 2.0 % and a negative bias of -1.01 %. Overall, the VW model under predicted the experimental results, whereas the hard sphere model over-predicted the experimental observations.

4.7.3 Asymmetric ternary mixtures of hydrocarbons over wide range of temperatures and pressures:

Also, Caudwell[10] extended the above study to ternary mixtures by adding a third component (propane) that is completely different from the other two. The addition of this light hydrocarbon gas resulted in making the mixture even more asymmetric because of the differences in molecular weight and physical state or phase of the added substance (propane). The viscosity and density of these ternary mixtures were measured on a total of about 206 data points in the temperature range between $298.15 \leq T / K \leq 473.15$ and pressures up to $p / \text{MPa} \leq 200$.

The experimental viscosity results were compared with the predicted values from the two models and the relative deviations were calculated as shown in Figures 4.3(a) and (b) below.

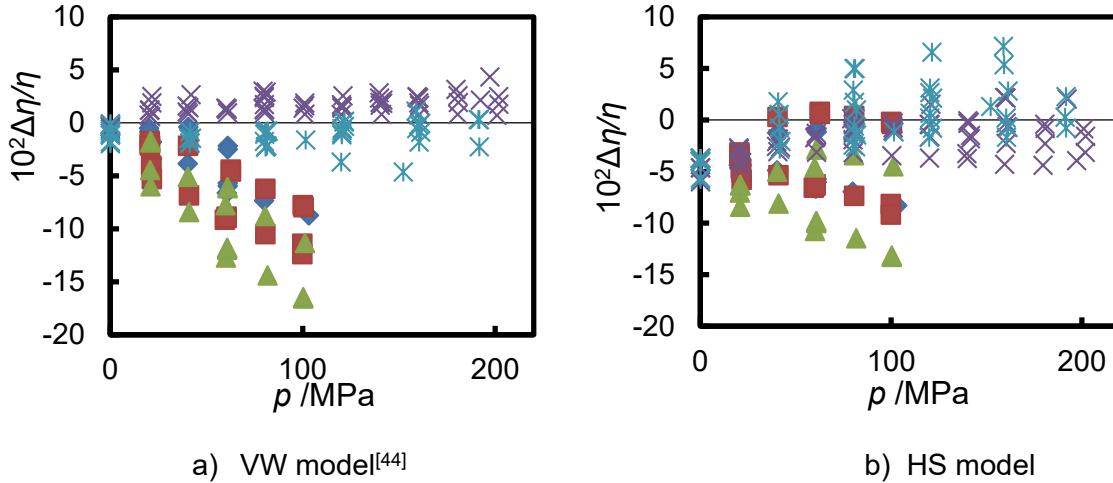


Figure 4.3: Relative deviations of VW and HS models from Caudwell[47]'s results (ternary) in the temperature range $298.15 \leq T / K \leq 400.00$ and pressures, $p / \text{MPa} \leq 200$.

✕, $x_1 = 0$, $x_2 = 1$ and $x_3 = 0$; ◆, $x_1 = 0.178$, $x_2 = 0.611$ and $x_3 = 0.211$; ■, $x_1 = 0.283$, $x_2 = 0.312$ and $x_3 = 0.405$; ▲, $x_1 = 0.425$, $x_2 = 0.344$ and $x_3 = 0.231$ and *, $x_1 = 0$, $x_2 = 0$ and $x_3 = 1$

From figure (4.6a) above, it can be seen that, the relative deviations of the VW model were distributed between -16.6 to +4.3 % with an $\Delta_{AAD,\eta}$ of 3.2 % and a negative bias of -1.9 %. On the other hand, the relative deviations of the hard sphere model were

distributed in the range from -13.3 % to +7.1 %, with an $\Delta_{\text{AAD},\eta}$ of 2.7 % and a negative bias of -2.6 % as shown in Figure 4.6(b). Overall, both models slightly over predicted the experimental viscosity of the mixture.

It is important to note that; the deviations of both models in the ternary mixtures were slightly higher than the corresponding deviations in the binary mixtures. This is due to the addition of a dissimilar component (propane), which makes the mixture even more asymmetric than the previous binary mixtures.

4.7.4 Asymmetric mixtures of hydrocarbon liquids with a dissolved supercritical component over wide range of temperatures and pressures

Several authors have studied extensively binary mixtures of methane + decane and as such, numerous experimental viscosity data are available in the literature, therefore, these datasets will be analysed to provide an insight to test the applicability of the VW and HS models for the estimation of the viscosity of asymmetric mixtures. For this system, about eight independent viscosity studies have been reviewed and for each of the study, separate viscosity data were calculated at the corresponding experimental conditions using the two models. Also relative deviations of the calculated values from the experimental observations were determined for all the datasets.

Peleties^[48] reported the experimental results of viscosity and density of binary mixtures of methane and *n*-decane at four compositions. Measurements were carried out on a total of 243 data points using a vibrating-wire viscometer-densimeter in the temperature range between $298.15 \leq T / \text{K} \leq 393.15$ and pressures up to 75 MPa. The experimental results were compared with the results predicted using the two models and the relative deviations of the predicted values were calculated and plotted against the pressure as shown in Figures 4.4(a) and (b) below.

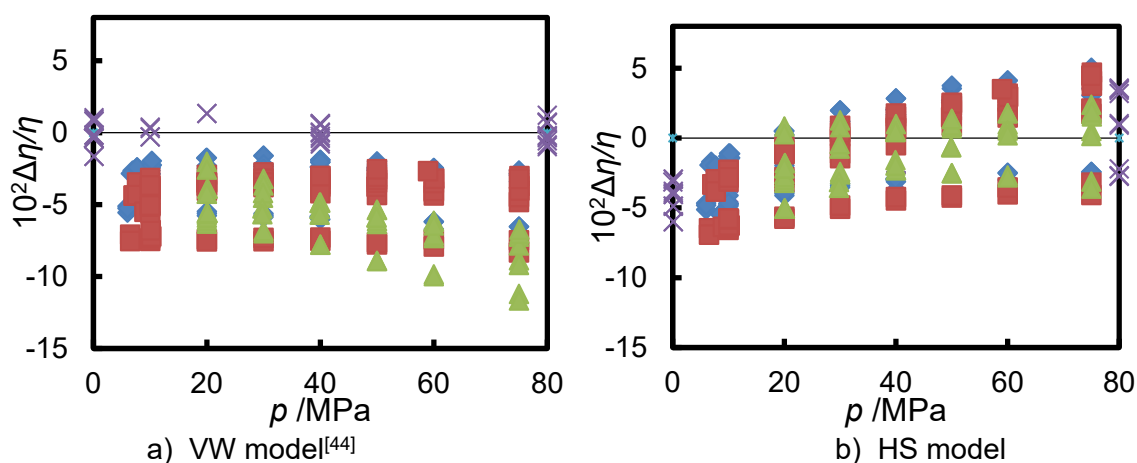


Figure 4.4: Relative deviations of VW and HS models from Peleties[48]' results at temperatures between $298.15 \leq T / K \leq 398.15$ and $p / \text{MPa} \leq 80$: $\times$, $x_1 = 0$; $\blacklozenge$, $x_1 = 0.252$; $\blacksquare$, $x_1 = 0.261$ and $\blacktriangle$, $x_1 = 0.429$

From Figures 4.4(a) and (b) above, it can be clearly seen that the deviations of the VW model predictions were distributed between $(-11.7 \text{ and } +1.3)\%$ with an $\Delta_{\text{AAD},\eta}$ of 2.2 % and a strong negative bias of about -3.8 %. On the other hand, the deviations of HS predictions were narrowly distributed in the range $(-6.9 \text{ to } 5.6) \%$ with an $\Delta_{\text{AAD},\eta}$ of 2.6 % and a weak negative bias of about -1.1 %. In addition, it was observed that the deviations were particularly larger at high methane composition and at higher temperature and pressure conditions.

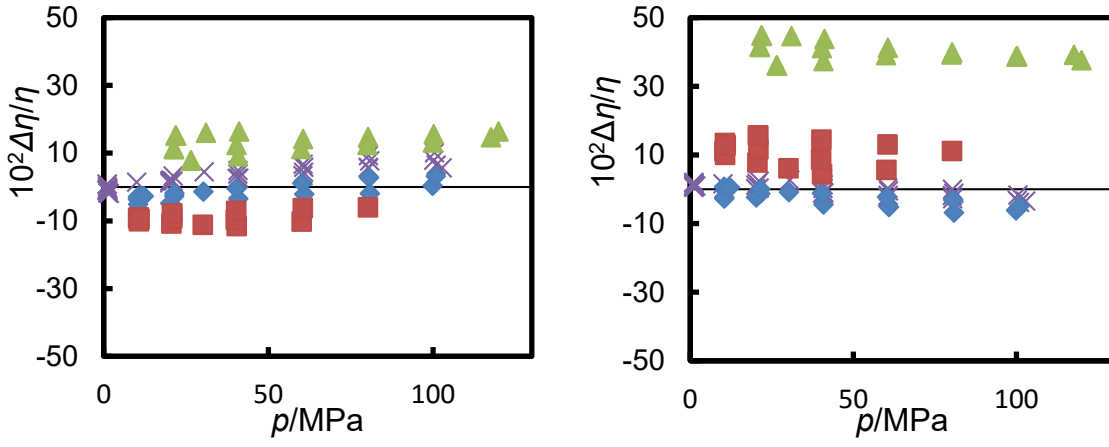
Even though both models over-predicted the experimental results (due to overall negative bias), however, in terms of the maximum and the span of the deviations, for this particular data the hard-sphere's predictions were relatively closer to the experimental data than those of the VW model.

Similar plots were made for the remaining seven (7) studies in this category as shown in appendix (A)

4.7.5 Highly asymmetric mixtures of hydrocarbon liquid and a non-hydrocarbon gas over wide range of temperatures and pressures

Ciotta[11] conducted an experimental viscosity measurements on binary asymmetric mixtures of CO_2 + *n*-hexadecane. The measurements were carried-out using a vibrating-wire densimeter-viscometer capable of providing simultaneous measurements for density and viscosity within an estimated uncertainty of 2 % for viscosity and 0.02 % for density respectively. A total of 136 data points were measured along five isotherms in the temperature range $298.13 \leq T / K \leq 473.86$, and pressures up to 120.16 MPa for three CO_2 mole fractions in the range $0 \leq x_1 \leq 0.727$.

The experimental data were compared with predictions from the two theoretical models – the VW model and the HS model and relative deviations of these models were calculated and shown in Figures 4.5 (a) and (b) below

a) VW model^[44]

b) HS model

Figure 4.5: Relative deviations of VW and HS models from Ciotta[11]'s results in the temperature range $298.18 \leq T / K \leq 400.00$ and $p / \text{MPa} \leq 120$: $\times$, $x_1 = 0$; $\diamond$, $x_1 = 0.06903$; $\blacksquare$, $x_1 = 0.5877$ and $\blacktriangle$, $x_1 = 0.727$

From Figures 4.5(a) and (b), it is evident that the deviations of VW model do not follow any particular trend with increase in compositions of the light component (CO_2) and were distributed between -12 % to +17 % with $\Delta_{\text{AAD},\eta}$ of 7 % and a positive bias of 3 %. On the other hand, the deviations of HS model followed a systematic increasing trend with increase in CO_2 mole fractions as shown in Figure 4.8b. For instance, at lower CO_2 mole fractions $x_1=(0.06903$ and $0.5877)$ the relative deviations of HS model were contained between -9% and 16 %. However, as the CO_2 mole fraction increased to $x_1 = 0.727$, larger deviations up to 45 % were observed. Similarly, the $\Delta_{\text{AAD},\eta}$ of HS model (13 %) was found to be nearly twice that of VW model (7 %). In addition, it can be seen that both models under-predicted the experimental results with positive biases of 3 % and 10 % for VW and HS models respectively.

4.9 Summary

The predictive powers of the two models were analysed based on the three performance indicators namely: the average absolute relative deviation ($\Delta_{\text{AAD},\eta}$), the maximum absolute deviation ($\Delta_{\text{MAD},\eta}$) and the relative bias ($\Delta_{\text{Bias},\eta}$). The $\Delta_{\text{AAD},\eta}$ s and $\Delta_{\text{MAD},\eta}$ s are performance indicators that measure the degree of closeness of the predictions from the theoretical models to the true experimental observations. For all the systems discussed above, these performance indicators were plotted in Figures 4.6, 4.7 and 4.8.

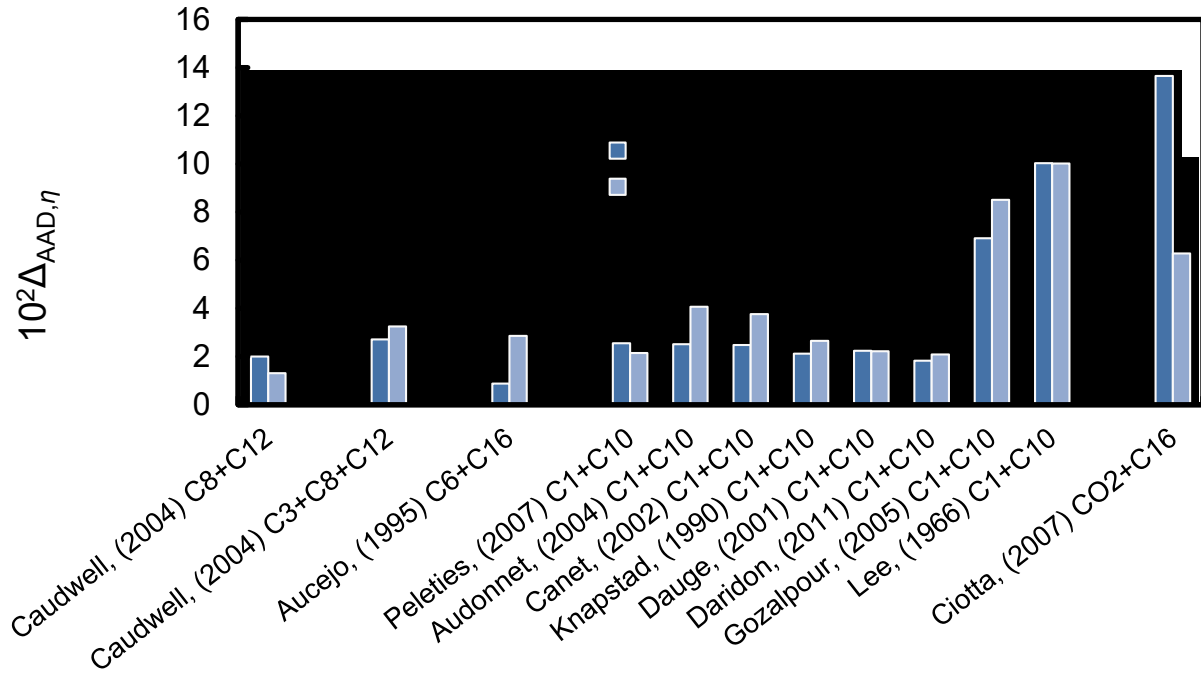


Figure 4.6: The Average absolute relative deviations $\Delta_{AAD,\eta}$ of VW^[44] and HS from experimental results of asymmetric mixtures

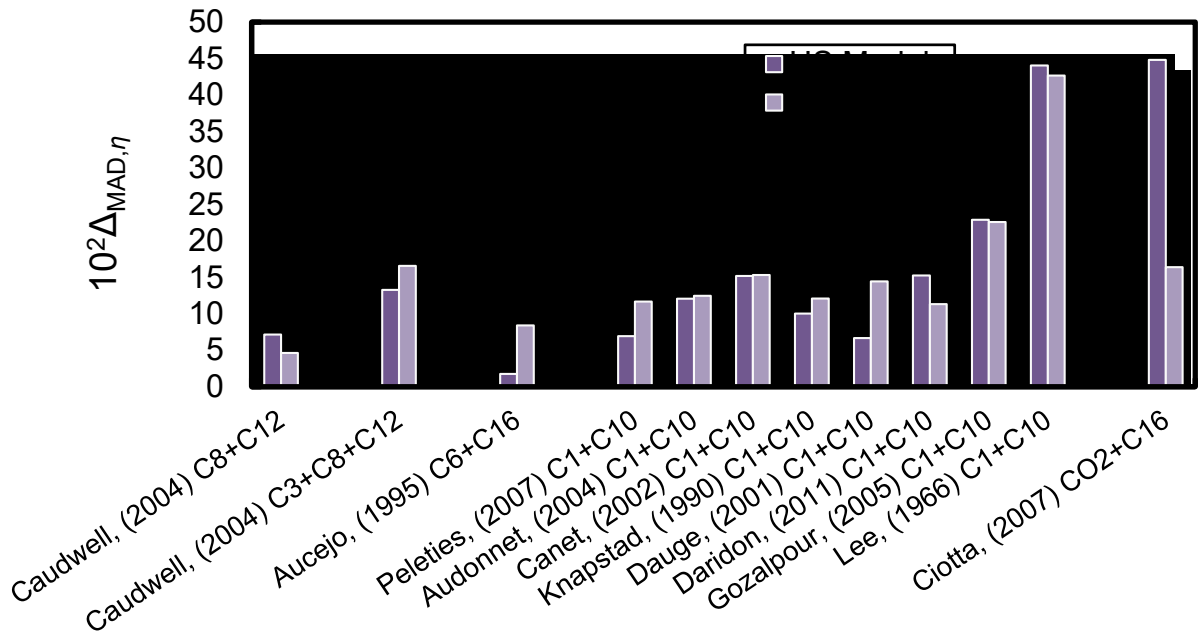


Figure 4.7: The maximum absolute deviations $\Delta_{MAD,\eta}$ of VW^[44] and HS models from experimental results of asymmetric mixtures

From the two figures above, it can be seen that, both $\Delta_{AAD,\eta}$ s and $\Delta_{MAD,\eta}$ s of the two models were similar for most of the systems considered in the analysis. The few exceptions to this were the binary mixtures of CO₂ + *n*-hexadecane studied by Ciotta^[49] and the liquid mixtures of *n*-hexane + *n*-hexadecane studied by Aucejo^[45]. In the former,

it was seen that both the $\Delta_{AAD,\eta}$, and the $\Delta_{AAD,\eta}$, of the HS model were more than twice their corresponding values for the VW model. This is partly attributed to the fact that the HS model lack suitable correlation for non-hydrocarbon fluids such as CO₂. On the other hand, for the latter system (i.e. *n*-hexane + *n*-hexadecane), it was observed that both the $\Delta_{AAD,\eta}$, and $\Delta_{MAD,\eta}$, of VW model were more than three times their corresponding values for the HS model, this is because the measurements were conducted at ambient conditions and the two model have different sensitivity to temperature and pressure conditions with the deviations of HS model depend so much on temperature and pressure conditions than those of the VW model.

Furthermore, close observation of Figures 4.6 and 4.7 revealed that both models consistently estimated the viscosity of binary mixtures of methane + *n*-decane with less than 4 % $\Delta_{AAD,\eta}$, and $\Delta_{MAD,\eta}$, better than 15 %. However, the large deviations seen in the data presented by Lee *et al.*[50] and Gozalpour *et al.*[51] were exceptions which could be attributed to some possibilities of error in their respective methods or equipment used for the measurements. For instance, Knapstad *et al.*[52] reported that the data reported by Lee *et al.*[50] deviated as much as 45 % from their results. For Gozalpour *et al.*[51]'s results, the large deviations in the viscosity were attributed to the fact that the author claimed that the measurements were conducted near the critical region at which they observed about 10 % viscosity increment upon approaching the saturation pressure of the mixture.

Also, the agreements of the experimental datasets described above with the predictions of the two models were analysed by plotting the systematic biases of datasets of the individual studies as shown in the Figure 4.8.

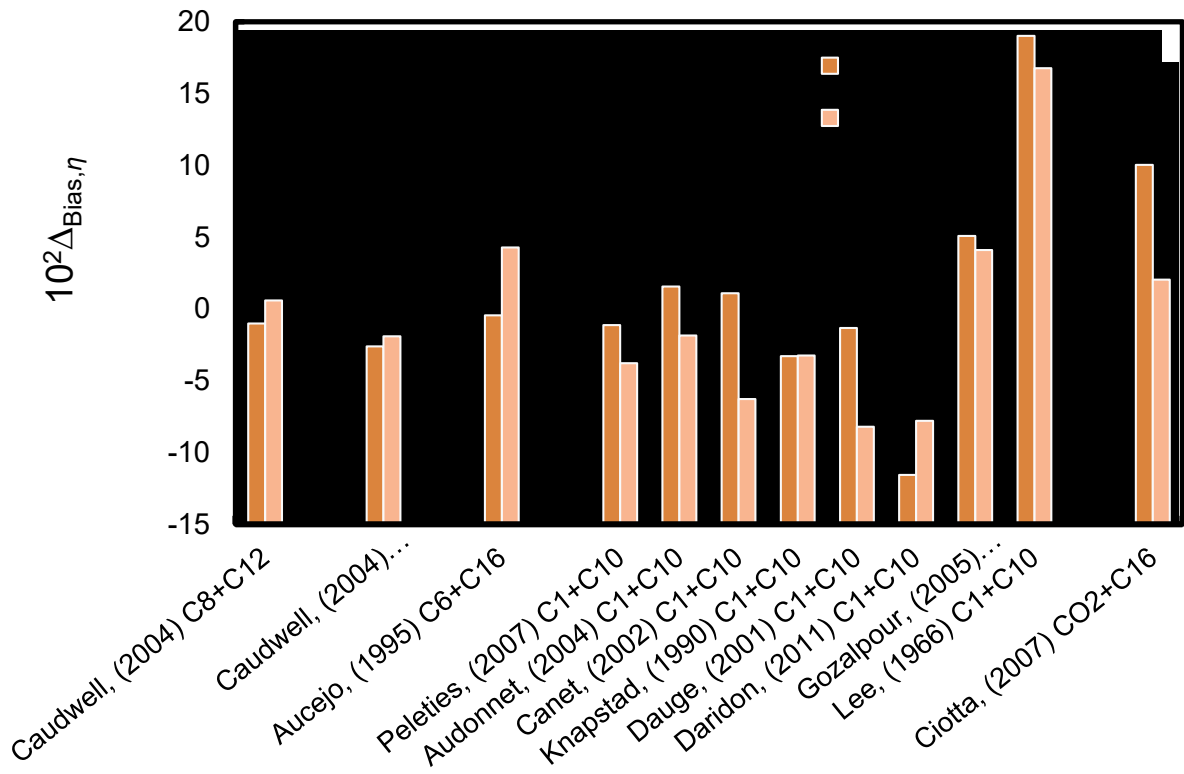


Figure 4.8: The average relative bias $\Delta_{Bias,\eta}$ of VW^[44] and HS models from experimental results of various asymmetric mixtures

It is evident from Figure 4.8 that both models over-predicted most of the datasets considered, this follows from the negative biases observed from the model predictions. On the contrary, the last three studies presented positive biases. Again this could be attributed to the reasons highlighted above.

Finally, all the deviations of the methane + *n*-decane mixtures were averaged and plotted on the same figure with the deviations from other systems as shown in Figures 4.9 and 4.10. This is to allow us compare the deviations of the two models on different fluid mixtures and to deduce any possible trend in the deviation with mixture's property.

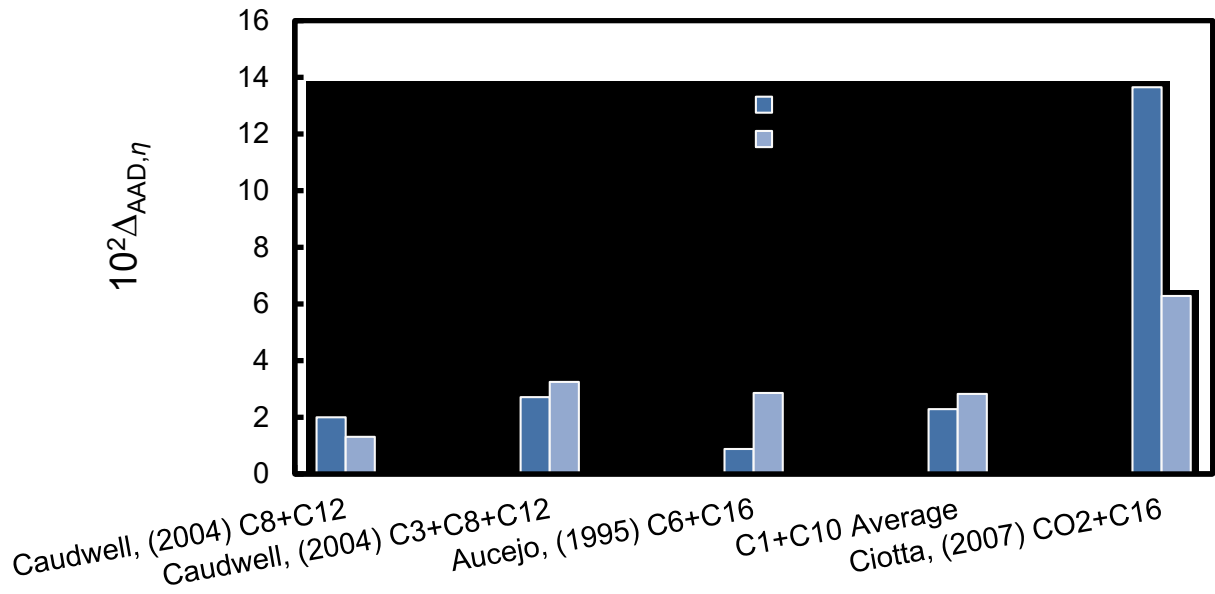


Figure 4.9: Average absolute relative deviations $\Delta_{AARD,\eta}$ of VW^[44] and HS models from experimental results of asymmetric mixtures

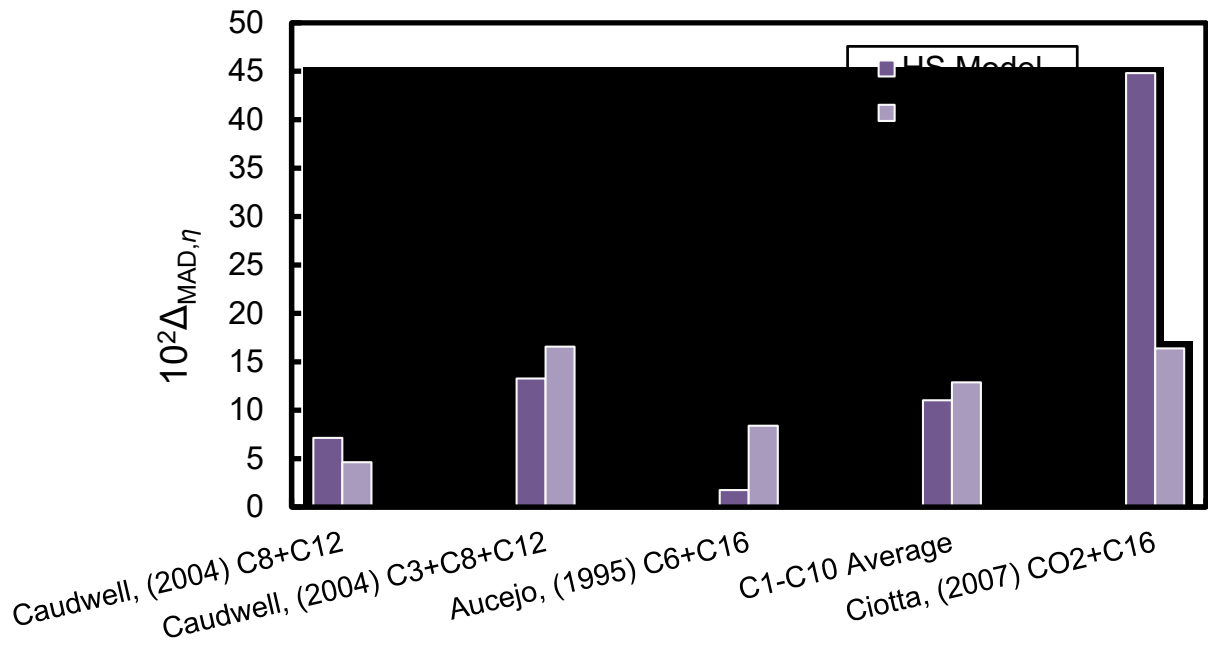


Figure 4.10: Maximum absolute deviations $\Delta_{MAD,\eta}$ of VW^[44] and HS models from experimental results of asymmetric mixtures

From both Figures 4.9 and 4.10, it is evident that the deviations of both models increases with increase in the degree of asymmetry of the mixture. For example, both $\Delta_{AARD,\eta}$ s and $\Delta_{MAD,\eta}$ s of the two models increases when dissimilar component (propane) was added to the binary mixtures of *n*-octane + *n*-dodecane studied by Caudwell[53]. Similarly, it was also discovered that the deviations of both models increases with increase in the molar mass ratios as well as the size and/or shape of the individual components of the mixture.

Furthermore, it was observed that the deviations of both models are particularly larger when the components of the mixture differ in nature (e.g. liquid, gas, hydrocarbon, non-hydrocarbon etc). This can be seen in the large deviations obtained from the mixtures of CO_2 + *n*-hexadecane in both figures.

4.9.1 Conclusions

Table 4.2 below summarises the deviations of the two models for the entire datasets considered in the analysis, and based on the statistical data presented in the table, the following conclusions can be drawn.

- For pure hydrocarbons, the results from both models were in good agreement with most experimental data investigated in this study.
- For simple liquid mixtures, both models satisfactorily predict the viscosity of the mixtures
- For asymmetric mixtures, the deviations of both models increases with increase in the degree of asymmetry of the components of the mixture
- For VW model due to its strong density dependence, large deviations were observed at higher molar density, whereas large HS deviations were seen at higher temperatures and pressures.

Table 4.2: Summary of $10^2\Delta_{AAD,\eta}$, $10^2\Delta_{Bias,\eta}$ and $10^2\Delta_{MAD,\eta}$ of VW^[44] and HS models in predicting the viscosity of some asymmetric mixtures

System/ Ref.	VW Mode ^[44]			HS Model			m.m ratio
	$10^2\Delta_{AAD}$	$10^2\Delta_{Bias}$	$10^2\Delta_{MAD}$	$10^2\Delta_{AAD}$	$10^2\Delta_{Bias}$	$10^2\Delta_{MAD}$	
C ₈ +C ₁₂ Caudwell ^[10]	1.39	0.54	4.63	2.88	-0.46	14.78	1.5
C ₃ +C ₈ +C ₁₂ Caudwell ^[10]	2.91	-1.31	16.57	3.38	-1.9	14.78	
C ₆ +C ₁₆ Aucejo <i>et al.</i> ^[45]	2.86	-4.28	8.40	0.88	-0.45	1.76	2.6
CO ₂ +C ₁₆ Ciotta ^[11]	6.52	2.79	16.72	12.88	10.31	44.81	5.1
C ₁ +C ₁₀ Peleties ^[48]	2.15	-3.78	11.67	2.55	-1.12	6.92	8.9
C ₁ +C ₁₀ Padua <i>et al.</i> ^[54]	4.07	-1.85	12.46	2.65	-0.17	8.98	8.9
C ₁ +C ₁₀ Canet <i>et al.</i> ^[55]	3.76	-6.28	15.32	2.48	1.09	15.19	8.9
C ₁ +C ₁₀ Knapstad <i>et al.</i> ^[52]	2.86	-3.73	12.09	2.45	-3.82	10.58	8.9
C ₁ +C ₁₀ Dauge <i>et al.</i> ^[56]	2.22	-8.20	14.43	2.24	-1.32	6.67	8.9
C ₁ +C ₁₀ Daridon <i>et al.</i> ^[57]	2.09	-7.79	11.32	1.83	-11.56	15.26	8.9
C ₁ +C ₁₀ Gozalpour, <i>et al.</i> ^[51]	8.51	4.10	22.58	6.91	5.09	22.90	8.9
C ₁ +C ₁₀ Lee, <i>et al.</i> ^[50]	9.22	16.3	42.66	9.42	17.77	44.05	8.9
C ₁ + C ₁₀ Average	2.85	-1.40	12.88	2.37	0.745	10.60	
Systems Investigated in this work				Systems Investigated in this work			
C ₁ +cC ₁₆	11.56	11.06	30.83	23.25	21.48	47.54	5.3
C ₁ +C ₁₆	9.79	9.19	25.27	35.91	35.91	63.14	14.1
C ₁ +bC ₃₀ H ₆₂	-	-	-	22.61	19.09	64.74	25.6

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Experimental Apparatus and Methods

5.1 Introduction

This project involved high-pressure, high-temperature experimental measurements of density and viscosity on representative asymmetric hydrocarbon mixtures using a vibrating-wire device. There were two different configurations of vibrating-wire viscometer available for this purpose. The first one was the vibrating-wire with a buoyant mass (BM) attached to one of its ends and, the second type was the vibrating-wire clamped (2C) at both ends. Both viscometers were used at different stages of the project, thus a brief description of both configurations will be given in the subsequent sections.

5.2 Vibrating-wire viscometer with a buoyant mass

This viscometer is used for simultaneous viscosity and density measurements and, as such, it is referred to here as a vibrating-wire viscometer-densimeter (VWVD) and it is the one used for the measurement of viscosity and density of both pure components and binary mixtures investigated in this work. As the name implies, the VWVD consisted of a vibrating-wire (VW) made from tungsten (Metal Cutting Corp. New Jersey, USA) of about 65 mm long and about 0.15 mm diameter, placed between poles of permanent magnets with magnetic field strength of about 0.3 T. The VW is clamped at the topside and tensioned by an aluminium buoyant mass (sinker) at the bottom. Tungsten was chosen as the wire material due its high tensile strength and Young's modulus, whereas aluminium was selected as the sinker material for better sensitivity to buoyant forces when immersed in the fluid therefore permitting accurate density measurement of the fluid surrounding the sinker. The equipment set-up as shown in Figure 5.1 consisted of three major units: the fluid handling unit; the accumulator (PulseGuard Ltd, Model PiG-SS); and the pressure cell housing the vibrating-wire assembly. These units were all situated in temperature controlled zones.

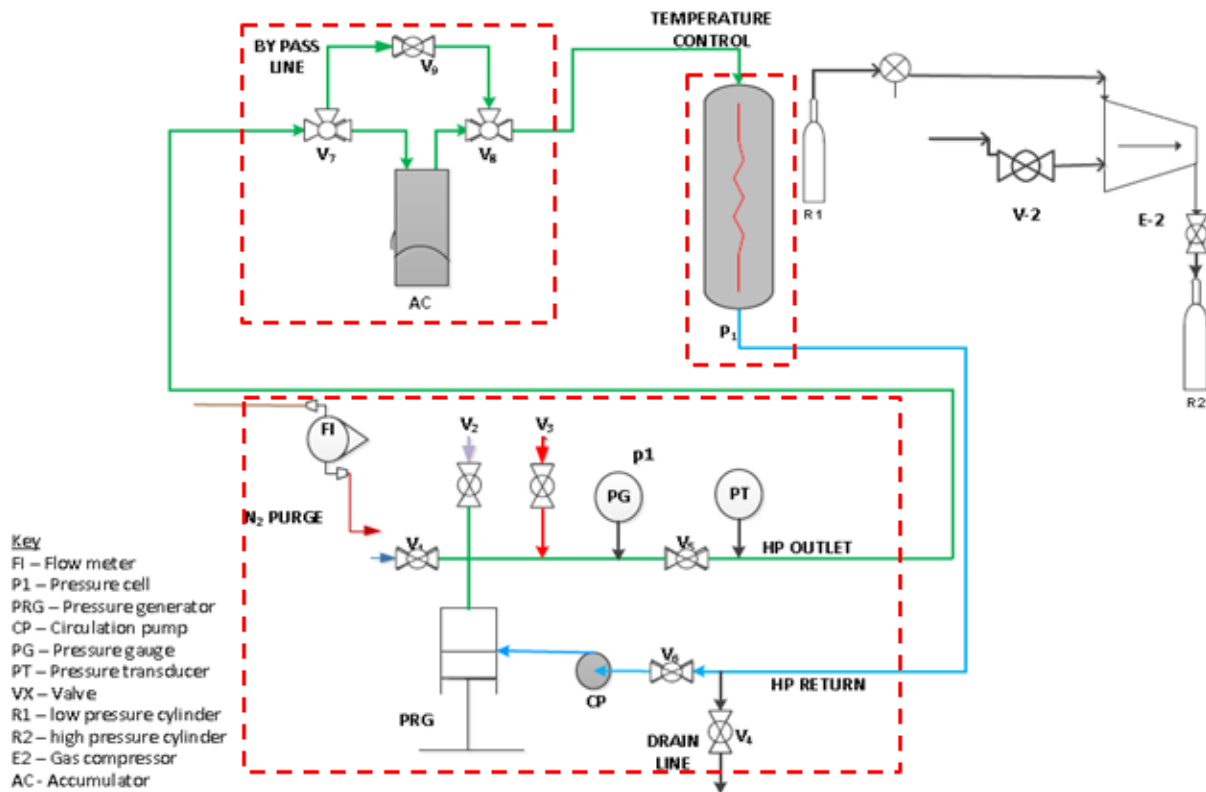


Figure 5.1: Schematics of the 2 kbar vibrating-wire viscometer-densimeter (VWVD)

5.2.1 The fluid handling unit

The fluid handling unit is an important part of the VWVD installation as it was used for many purposes during measurement. Some of the functions of this unit include: to fill/drain the system, to homogenise the fluid when dealing with mixture of components of different phases and also, to pressurise the system to the desired pressure value. The unit as shown in Figure 5.1 comprised of the following major components.

- SITEC (2 kbar) screw injector
- Pressure gauge
- Pressure transducer
- Magnetic circulation pump
- Flow meter for nitrogen purge
- Two 150 W finned-strip Watlow heaters
- Thermocouple sensors
- Safety devices (I.e. the bursting disc and low pressure proportionate relief valves)

5.2.2 The pressure cell

The cell was a monoblock cylindrical stainless steel vessel that serves as a container for the fluid under study. It also housed the vibrating-wire, the magnet assembly and the buoyant aluminium mass as shown in the figure below. The cell was rated for application

at maximum working pressure of 2 kbar at 473 K. The revised detailed-design calculations of the dimensions of the cell as well as a comprehensive stress analysis and report are presented in appendix C.

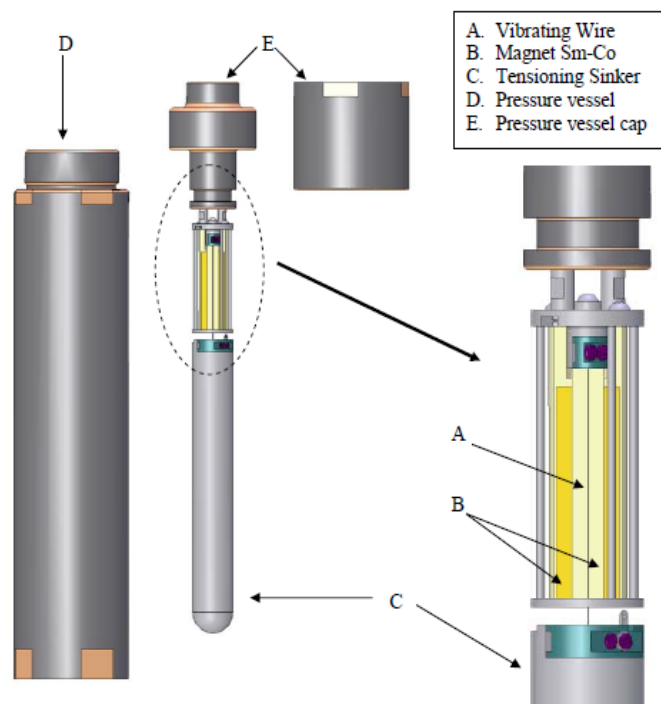


Figure 5.2: The pressure vessel and the vibrating wire assembly of the 2 kbar VW viscometer^[1]

5.2.3 The Signal detection and processing unit

The voltage across the vibrating-wire was detected by means of a lock-in amplifier (SR830 DSP) which was connected to a computer via GPIB interface. The lock-in amplifier also provided a steady state voltage which was then converted into a constant current by means of a fixed (1.4 K Ω) resistor connected in series to the vibrating-wire as shown in the figure below.

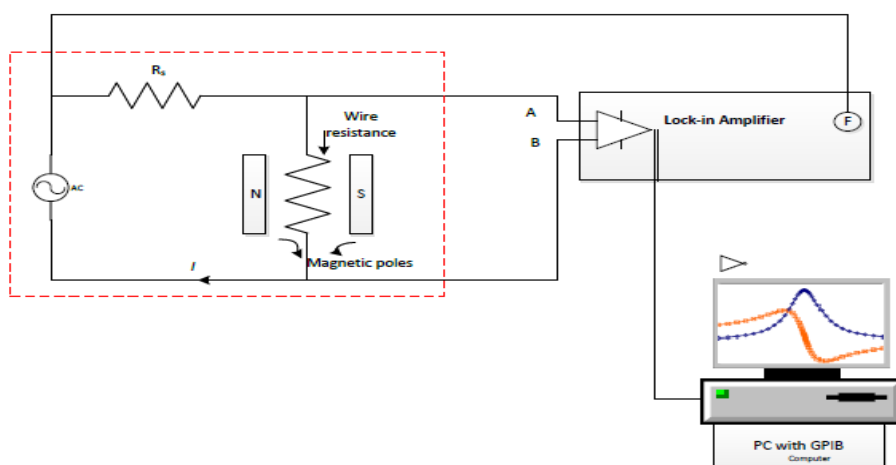


Figure 5.3: The electrical circuit diagram of the vibrating wire device

5.2.4 *Temperature and pressure control*

The pressure cell was heated by ten 110 W cartridge heaters with total maximum power of 1100 W positioned in three distinct zones: top, middle and bottom sections of the aluminum block housing vessel. The top and bottom sections contain two heaters each, whereas the middle section contains six heaters connected in parallel. The heaters were controlled by means of a three-channel PID controller that regulated the temperature in these zones. The overall temperature of the cell was measured using a platinum resistance thermometer (PRT) which was inserted into a thermowell bored in the cap of the pressure vessel. This PRT was calibrated both at the triple-point of water (TPW) in a water triple-point cell and also at temperatures in the range (313 to 433) K in oil bath by comparing against a standard PRT which in turn was calibrated on ITS-90[2] at the United Kingdom (UK) National Physical Laboratory[3]. The overall expanded uncertainty in temperature measurement was within 0.02 K at a coverage factor k , of 2.

The system was pressurized by means of hand-driven pressure-generator (Sitec-Sieber Engineering AG, model 750.1200) and the pressure was measured using a sensor (GT1600) from Stellar Technology Inc. and the estimated expanded uncertainty in pressure measurements was within 0.02 MPa with a coverage factor k of 2

5.3 **Vibrating-wire clamped at both ends**

The vibrating-wire in this set-up was made from a thin metallic alloy (90% Pt and 10% Ir) clamped at both ends. This arrangement causes the device to lose the needed sensitivity for density measurement and as such, a separate inline vibrating-tube densimeter was connected in the system to provide the density input required in the viscosity calculation. The vessel housing the vibrating-wire was designed to a maximum working pressure of 100 MPa at 448.15 K and it was fabricated from hastelloy material in order to permit measurements on aqueous systems. The set-up consists of the following major components as shown in the below.

- Vibrating-wire viscometer
- Vibrating-tube densimeter
- Circulation pump
- Quizix pump
- Petite fleur temperature controller
- Huber Mini chillers
- Gas booster

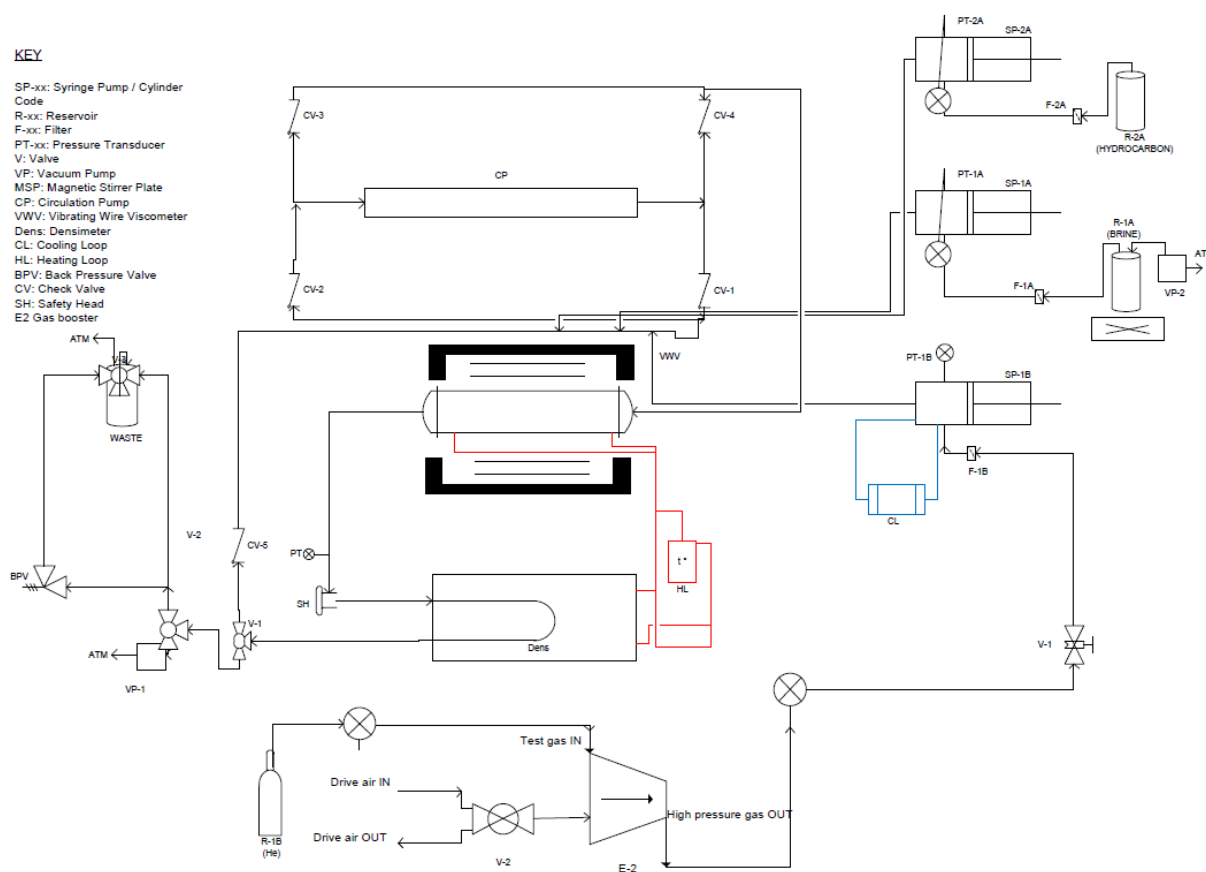


Figure 5.4: Schematic flow diagram of the 1 kbar VWV-VTD device^[4]

5.4 Incremental improvement and experimental procedure

To facilitate the use of the 2 kbar vibrating-wire viscometer-densimeter VWVD in measurements on flammable mixtures and also to ensure strict compliance with the relevant safety standards, several modifications were implemented on the existing VWVD apparatus. Some of the major improvements are highlighted below.

5.4.1 Review of design calculation and provision of a revised design report

To begin with, a critical review of the design calculations of the 2 kbar pressure cell housing the vibrating-wire assembly was conducted and a revised design report (reproduced in appendix C) was prepared. This was necessary in order to enable registration of the vessel in compliance with the College's regulations on pressure system safety regulations (PSSR) and pressure equipment regulations (PER, UK version of PED) which require all pressure equipment that operate at a gauge pressure $p > 50 \text{ kPa}$ and/or pressure-volume product $p \cdot V > 5 \text{ kPa} \cdot \text{m}^3$ be registered with insurance inspectors.

5.4.2 Replacement of all the electrical cables and insulation materials in the fluid handling systems

In order to avoid the risk of electrical shock, all the electrical cables in the fluid handling unit were replaced with the ones of adequate voltage ratings, and additional insulation materials were put in-place at more vulnerable joints. This would ensure smooth passage of current to the heating elements in the unit as well as to serve as a precaution to prevent the risk of electric shock to the operator in the event of oil spills on the metal part of the valve box.

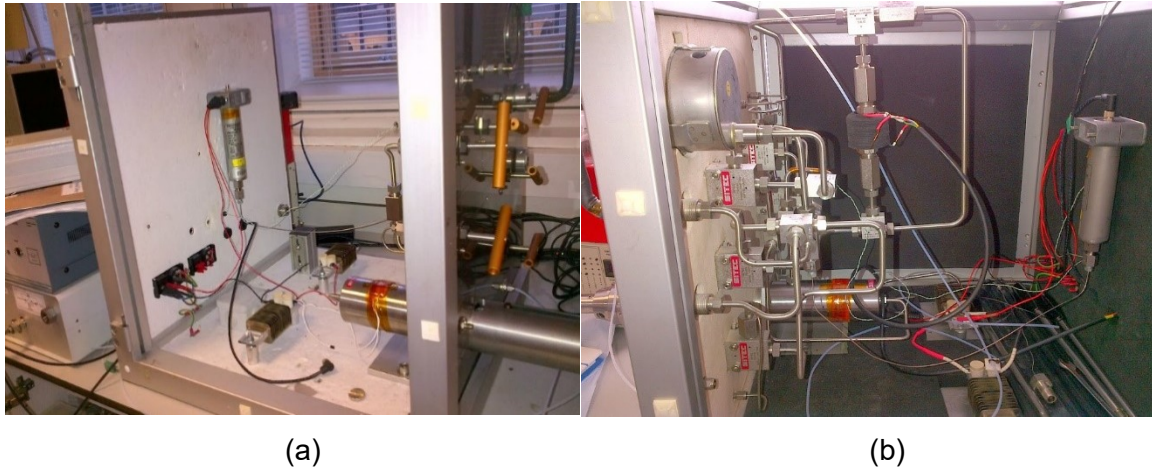


Figure 5.5: Pictures of the valve box in the fluid handling unit (a) before and (b) after the replacement of the insulations and electric cables.

5.4.3 Incorporation of two inert gas (Nitrogen) purging units

Two nitrogen-purging systems have been installed in the FHU and the accumulator vessel in order to keep them dry and to avoid unwanted accumulation of flammable fluid in the valve box.

5.4.4 Installation and testing of magnetic circulation pump

When conducting measurement on mixture of liquid and gas, it was necessary that the mixture is homogenized and brought to a single liquid phase before the measurement was commenced. To achieve this, a magnetic circulation pump was installed in the fluid handling unit. The pump design which has been described in detailed by Ciotta^[1], consisted of a high-pressure cylinder of 3/8" external diameter and about 100 mm long which was honed to an internal diameter of 5.2 mm. The piston was made from a magnetic stainless steel type 431, in form of a hollow cylinder with diameter of about 5.15 mm, an internal bore of 2 mm diameter, and about 32 mm long. The top of the piston was machined to form a conical seat that served as a check valve, and a second check valve was positioned at the top end of the nipple by means of an O-ring. Furthermore, this pump was fully tested by determining the optimum combination of frequency and amplitude at which it gives a maximum throughput. It was found that the pump delivered

the highest volume of 50 ml of isopropanol in one minute when the drive voltage was set to 10 volts and the frequency set to the highest value of 4 Hz. Figure 5.6 shows the magnetic circulation pump under test operation whereas Figure 5.7 shows the calibration curve for the circulation pump.

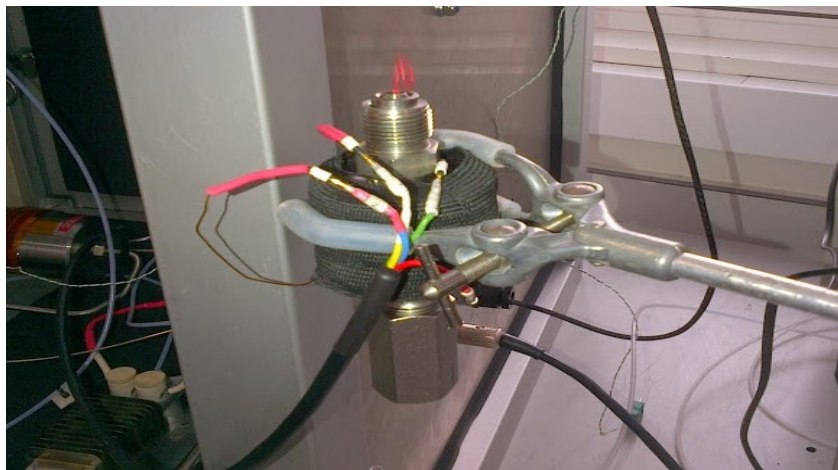


Figure 5.6: Picture of the new recirculation pump being tested and installed

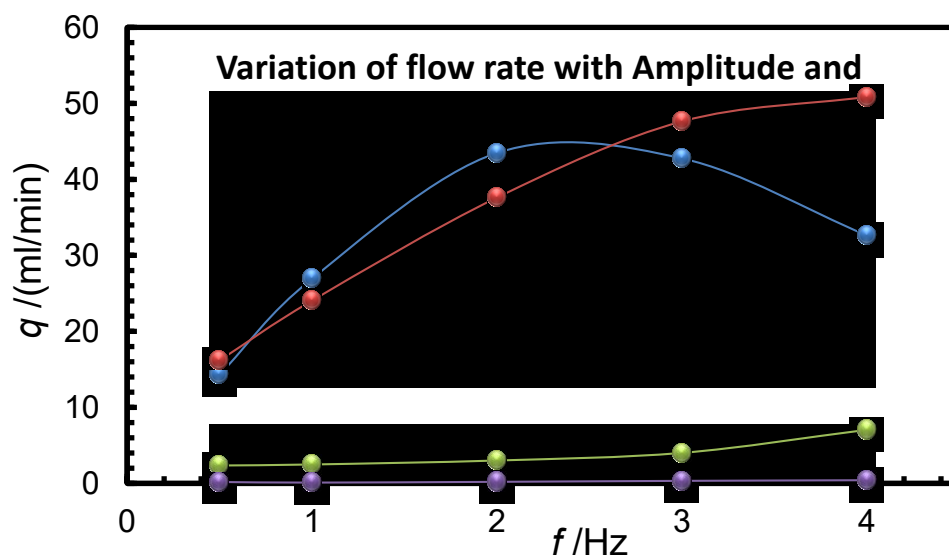


Figure 5.7: Plot of the sensitivity analysis to determine the optimum combination of amplitude and frequency that gives the maximum throughputs. —●—, amplitude = 10 Volt; —●—, amplitude = 8 Volt; —●—, amplitude = 5 Volt and —●—, amplitude = 4 Volt

5.4.5 Design, Installation and commissioning of magnetic circulation pump

After several measurement circles with the circulation pump described in section 5.4.4, above it was observed that the mixture in the system was poorly mixed and this was evident from the measured viscosity values. We then discovered a number of problems with the circulation pump which include: the pump body gets extremely hot after long hours of operation; the piston due to its vertical orientation persistently gets stuck at the top of the pressure nipple; the O-ring on the check valve worn-out overtime and above all,

the pump has become too weak to homogenize mixtures involving heavy components such as squalane effectively. To overcome these challenges, we decided to switch to a more robust design of a circulation pump similar to the one described by Peleties *et al.*^[5]. This is a pneumatically operated reciprocating pump that consists of a stainless steel SITEC high-pressure nipple of 200 mm long and outside diameter of 14.3 mm and an internal bore of 4.8 mm. The internal diameter of the nipple was honed to 5.00 ± 0.01 mm. Furthermore, the two ends of the nipple were counter-bored by half a mm of a diameter to a depth of 2 mm to prevent the piston from getting stuck at the ends. A piston of 40 mm long was fabricated from a magnetic stainless steel rod grade 431 and designed to a clearance of 0.3 mm from the internal diameter of the high-pressure nipple. This piston was allowed to travel with the magnetic assembly along the length of the nipple.

The two ends of the pressure nipple were connected to an unequal tee piece to which two check valves are attached to each. The check valves direct the flow from both sides of the piston to the top section of the pump and ultimately, back to the pressure generator for re-injection and continuous mixing. Figure 5.8(a) shows the solid works assembly and (b) shows the picture of the pump after the actual assembly. The pump was fully tested with cyclohexane and it was found to deliver at a flow rate of $1.9 \text{ cm}^3/\text{s}$ when the air-dive regulator was set to 1 bar and the speed controller (SMC, AS1002F-04) was set to about 6 needle-rotations.

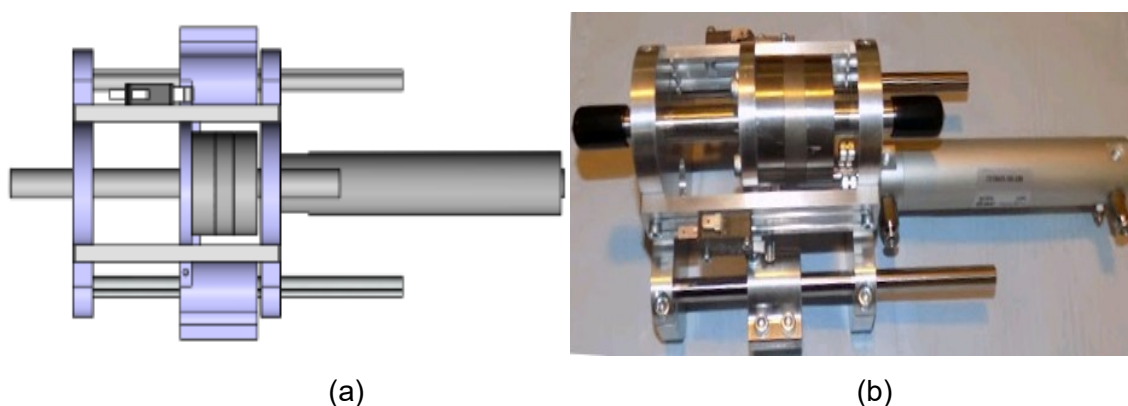


Figure 5.8: Design of a new magnetic circulation pump (a) solidworks assembly and (b) picture of the final assembly of the pump

5.4.6 Incorporation of safety relief valves and extension of outflow from the system to the main drain line in the laboratory.

To improve the safety of the system, low-pressure proportional relief valves were installed on both the vacuum line as well as the gas inlet lines in the fluid handling unit. This was done to prevent against over-pressurizing the vacuum pump and also, to protect the gas inlet from back pressure. In addition, the outflows from these relief valves and main system were extended and connected to the main drain line in the laboratory which was

re-routed outside to avoid discharging flammable/hazardous fluids to the laboratory environment.

5.4.7 Design and construction of a new aluminum weight for use in the pressure vessel

For safety considerations, it was beneficial to reduce the volume of the sample fluid by reducing the net volume of the pressure vessel, this was achieved by constructing a bigger aluminum weight than was previously used. The new weight was fabricated from aluminium grade T3 in cylindrical shape having a diameter $d = 30.3$ mm and height $h = 197$ mm with a 1 mm chamfer at the bottom end (see Figures C.6 and C.7 in appendix C for the detailed Engineering drawings). The sinker having this dimension reduces the net volume of the pressure vessel as well as the clearances between the sinker and the vessel internals. From the lower end of the sinker to the bottom of the vessel, the clearance has been reduced to less than 1 mm depending on the length of the vibrating-wire installed and also on the working temperature. For instance, it was discovered that for a tungsten wire of 64.91 mm long, the bottom clearance could be reduced from 0.77 mm at $T = 323$ K to about 0.24 mm at $T = 473$ K due to the differential expansion between the stainless steel pressure vessel and the aluminium sinker. Aluminium was chosen as the material for the sinker for better sensitivity to the buoyant forces when immersed in a fluid. The new weight was anodized (as shown in Figure 5.9) as a means to inhibit any corrosion effect that might occur on the surface of the sinker and also to insulate it from conducting electricity.



Figure 5.9: Newly designed, fabricated and anodized aluminium sinker

5.4.8 Calibration and installation of new pressure transducer

A new strain-gauge transducer (Stellar Technology Inc., model GT1600 series) was purchased to replace the damaged pressure sensor previously installed in the fluid handling unit. The GT1600 has a full-scale pressure up to 30000 psi (206.84 MPa) and combined high static accuracy (about 0.1 %) with high level output. In addition, it provided the flexibility of selecting wide range of current outputs (4 to 20 mA), numerous voltage outputs and also can be interfaced with many digital outputs including RS232, RS485 and CANbus. Similarly, a new digital display model E725 compatible with the GT1600 transducer was purchased from RDP Electronics. The new transducer GT1600 and the E725 display were calibrated at two extreme pressures (i.e. vacuum where $p = 0$ MPa and at the full scale pressure $p = 200$ MPa) using the Hydraulic Dead-Weight Tester. This is to ensure that the display accurately reads the pressure readings from the transducer.

Although the GT1600 was supplied with a calibration certificate from the manufacturer, it was recalibrated at full-scale pressure at two temperatures (i.e. 295.25 K and 313.15 K) using a Hydraulic Dead-Weight Tester model (DH-Budenberg 580 EHX) shown in Figures 5.9. This was to verify the accuracy of the transducer as claimed by the manufacturer and also to determine any hysteresis at the highest working temperature of the sensor in the fluid handling unit. It was found from this calibration that the accuracy of the transducer is in fact better than the 0.1 % as claimed by the manufacturer and the hysteresis is almost negligible at the highest working temperature of interest. The calibration data are presented in appendix C whereas, Figure 5.10 shows the calibration plot and the combined deviation plots for both our calibration data and the manufacturer's data whereas Tables B.17(a) and (b) in appendix B present the calibration data.

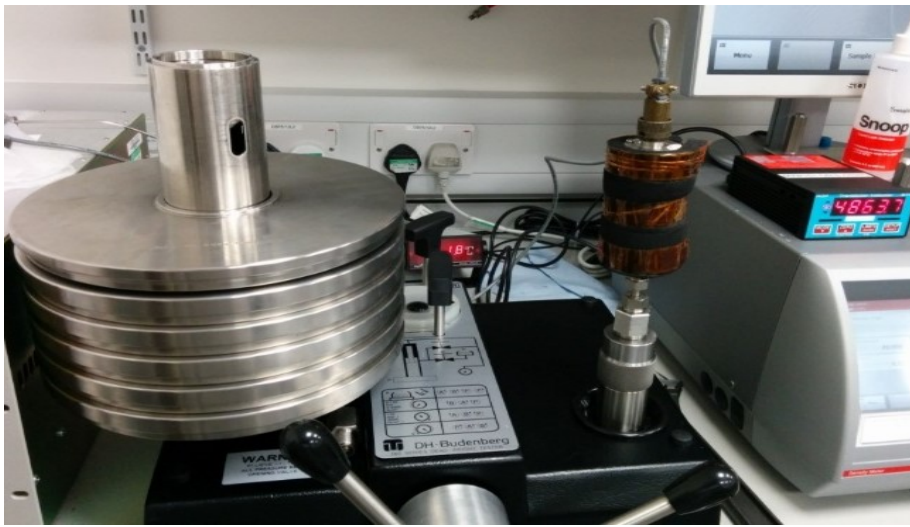
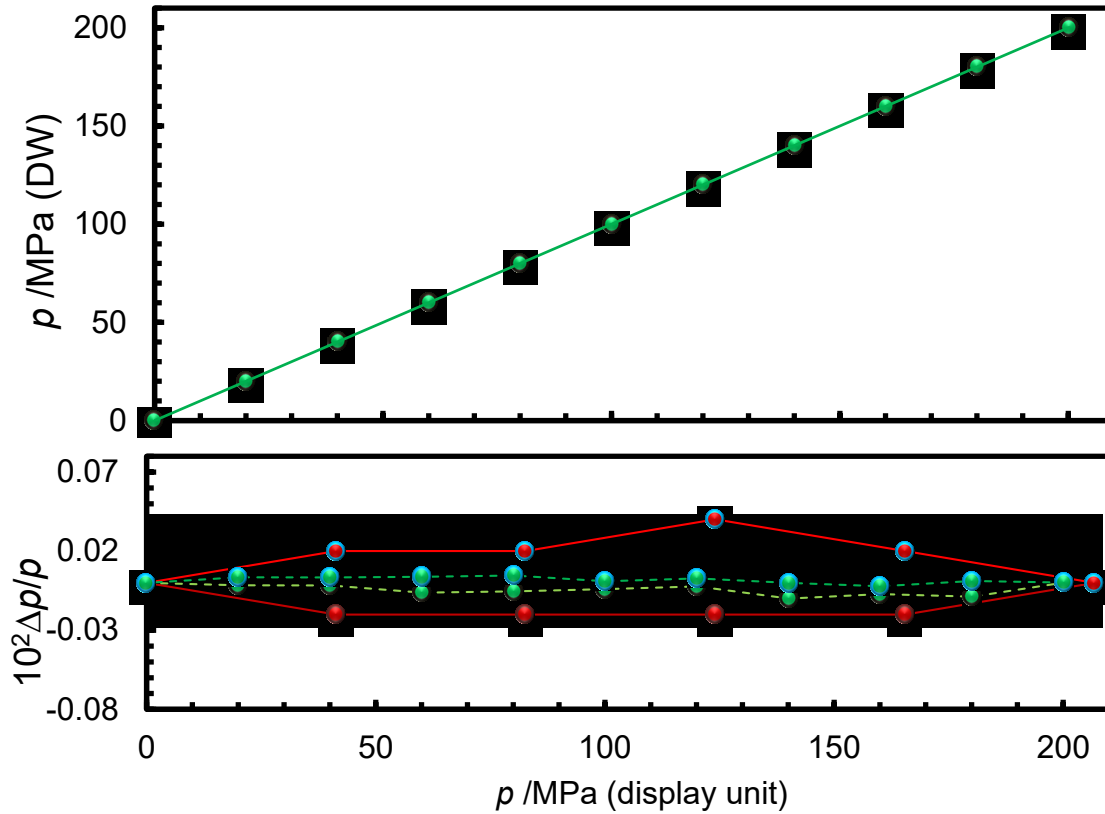


Figure 5.10: Dead-weight tester set up for the calibration of the new pressure sensor



Figures 5.11: Calibration curve and comparison of our calibration with the standard uncertainties from the manufacturer's calibration. The green symbols denote our calibration whereas the red symbols represent the manufactures calibration data

5.4.9 Replacement of the heated tubes in the 1 kbar Vibrating-Tube Densimeter Vibrating-Wire Viscometer (VTD-VWV)

Following the poor quality results obtained from the first VTD calibration, it was discovered that there was a significant heat loss around the densimeter and the flow lines of the 1 kbar VTD-VWV. To minimize these losses, the insulations around both the viscometer and the VTD densimeter were adequately improved. In addition, the insulations around the flow lines were completely replaced with new material and improved heating wire connections as shown in Figure 5.12 below

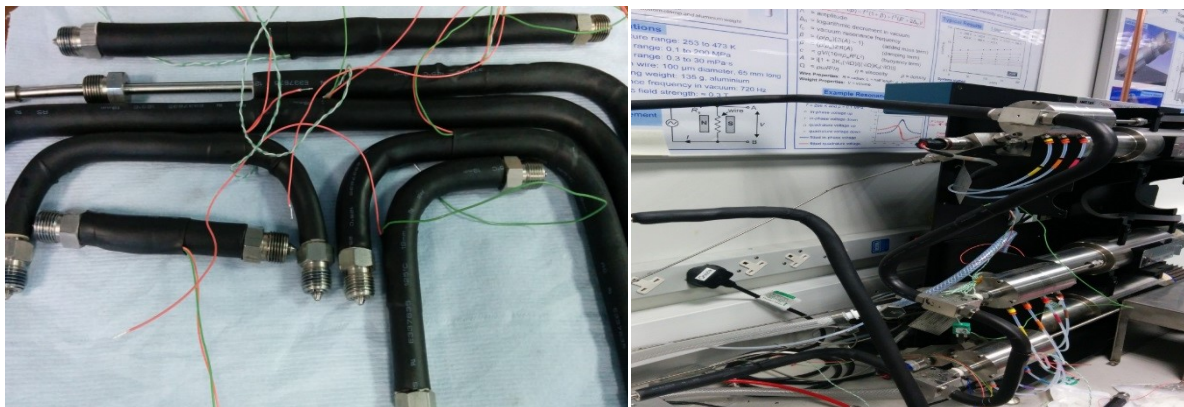


Figure 5.12: Improved insulations on the flow lines of the 1 kbar VTD-VWV

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Operating Procedure

6.1 Introduction

In both vibrating-wire viscometers, the measurement is conducted by passing an alternating electric current through the vibrating-wire element which, due to the presence of magnetic field, sets the wire into transverse oscillations. The width of the resonance peak and the resonance frequency of the oscillation depend respectively on the viscosity and density of the surrounding fluid. For instant, it can be seen from Figure (6.1) that the width of the resonance frequency obtained in liquid *n*-hexadecane is much wider than that obtained in ambient air, and this is because the former is more viscous than the latter. The signal measured by the lock-in amplifier is the sum of two voltages: the first one is the voltage due to the electrical impedance of the stationary wire; and the second is the induced voltage due to the motion of the wire. The measured signal was then fitted into the governing equation (3.57) of the device to evaluate both the viscosity and the density data of the surrounding fluid. Figure 6.1 illustrates a typical resonance frequency curve obtained in liquid *n*-hexadecane and air.

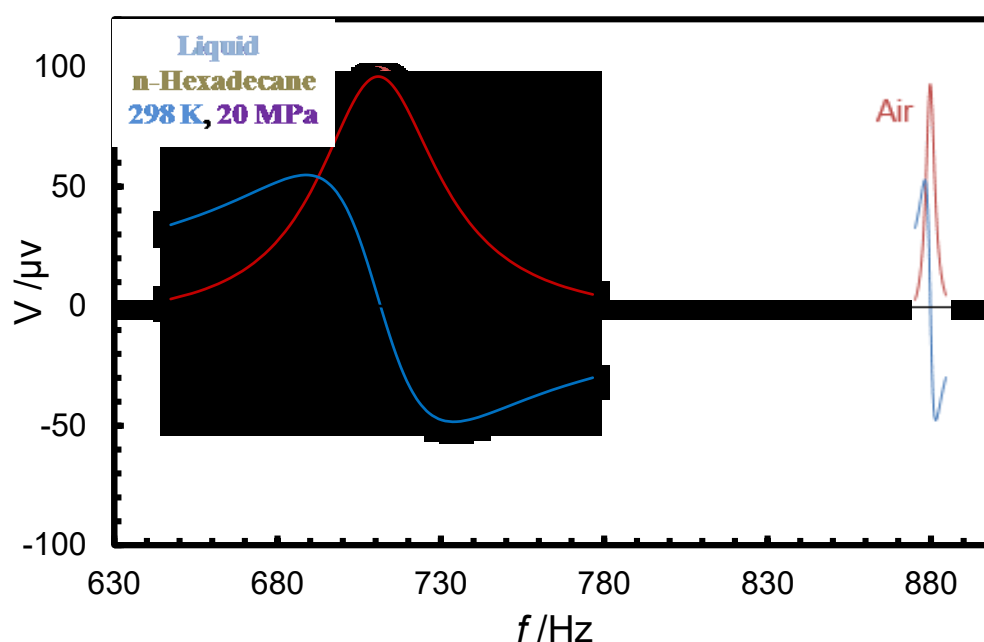


Figure 6.1 Typical resonance frequency curve obtained in liquid hexadecane at 298 K, 20 MPa and that of ambient air. ●, Red symbols denote the real parts of the experimental data and ●, blue symbols represent the imaginary part of the experimental data. Lines represent the model.

From Figure 6.1, it can be seen that the width of the resonance curve for the *n*-hexadecane is much wider than that obtained in air. This is as a result of the marked differences in viscosity of the two fluids.

Before any measurement is conducted, it is necessary that the VW device is thoroughly cleaned and calibrated (if operated in relative mode) to determine some physical constants (i.e. radius of the wire and volume of the suspended sinker) used in the working equations. The following section presents a brief description of the cleaning and the calibration processes. Detail description of the standard operating procedure is described in appendix D.

6.2 Cleaning

Prior to the commencement of any measurement, the VW equipment was cleaned and dried to avoid cross contamination of the samples during measurement. The cleaning process is itemized below.

- i. The system was evacuated of any existing fluid and then followed by flushing several times with compressed air or inert gas such as nitrogen to get rid of any residual fluid
- ii. If water was involved at any stage of the operation (e.g. during calibration in the case of the VWV-VTD), appropriate solvent such 2-propanol was used to dissolve the traces of water in the system
- iii. The system was then washed thoroughly with a volatile solvent such as hexane
- iv. Step one was repeated to evacuate the solvent used in step (iii)
- v. Vacuum pump was then connected and allowed run for several hours to dry the system,
- vi. While under vacuum, the temperature of the system was raised to a sufficient degree to vaporise any residual solvent

6.3 Calibration

One of the advantages of the vibrating-wire viscometer is the flexibility to operate the device in both relative and absolute modes. In the relative mode, some of the properties of the wire and sinker are obtained via calibration in fluid of widely known properties. The calibration entails a process of determining the wire radius and the sinker volume by conducting a single point measurement in a fluid with known density and viscosity and, other parameters such as the logarithmic vacuum decrement Δ_0 and the empirical parameter a in the resonance frequency model are obtained from vacuum calibration or measurement in gas at low pressure. For the 2 kbar viscometer, usually a hydrocarbon based fluid such as decane was used to determine the radius of the wire and the volume of the suspended sinker. For the 1 kbar viscometer, since measurements were usually made on aqueous solutions, pure de-ionized water was used to determine the hydrodynamic radius of the wire. In both cases, measurements were conducted in the

calibration fluid at ambient conditions and the viscosity and density values of the calibration fluids were taken from a reliable literature source and then fitted to a model to obtain the wire radius and the sinker volume.

For most part of this research, the 2 kbar VWVD was used and measurements were conducted in absolute manner without any rigorous calibration. In this regards, the key parameters (i.e. wire and sinker properties) in the governing equations (3.50 to 3.60) were determined from direct independent measurements. The following sections highlight how these parameters in the working equations were obtained.

6.4 The wire properties

The properties of the vibrating-wire (i.e. length L , and radius R ,) are very important parameters in the viscosity determination using a vibrating-wire sensor and so, accurate determination of these parameters is paramount for accurate viscosity measurement irrespective of the mode of operation of the device. It is evident from equation 3.60 re-written in the following form

$$\eta = \frac{2\pi f \rho R^2}{\Omega}, \quad (6.1)$$

that, viscosity is directly proportional to the square of the radius of the wire and so, and any uncertainty in determining the radius of the wire would be translated in the viscosity value itself. In view of the sensitivity of the radius of the wire, many laboratories choose to determine this property via calibration in a fluid of well-studied viscosity as highlighted in the previous section. On the other hand, when it is possible to obtain the wire properties from direct measurement with sufficient accuracy, the VWVD sensor could be operated in absolute mode. In this work, we operated the sensor in an absolute manner and the wire properties were determined from direct mechanical measurement. In this regard, the wire diameter (and hence the radius) was determined from repeated measurements conducted with a laser micrometer (Aeroel SRL, model XLS13XY) shown in Figure 6.2(a) and the length of the wire was measured with an internal caliper (Kroeplin, model H260) shown in Figure 6.2(b) calibrated against a 70 mm i.d. setting ring. The wire diameter was measured at three different planes (i.e. Φ_x , along x-axis, Φ_y , along y-axis and at 90° perpendicular to the wire and the average of these values were taken.

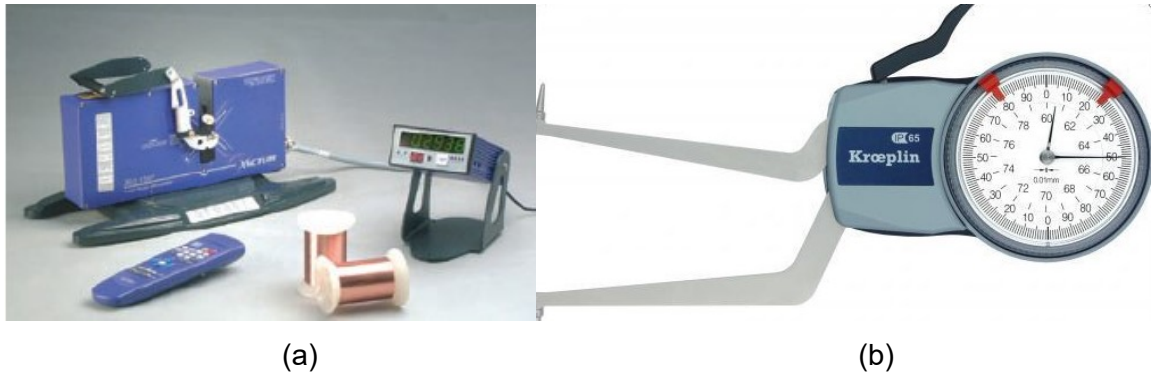


Figure 6.2(a), the laser micrometer used to measure the diameter and (b) the internal caliper used for measuring the length of the vibrating-wire

Other properties of the wire such as the density and Young's modulus were obtained directly from the literature data of the wire material. The density of tungsten as calculated from the lattice parameter $a = 3.16522 \pm 0.00009 \text{ \AA}$ at 298 K is $19254 \text{ kg}\cdot\text{m}^{-3}$ as given by Parrish *et al*[1]. The Young's modulus E , and its temperature dependence coefficient ϵ , were obtained by considering several literature data [2-8] on the elastic constant for both single and polycrystalline tungsten material. Figure 6.3 shows the ratio of Young's modulus E of both single and polycrystalline tungsten at a given temperature to the corresponding values at 300 K, E_{300}

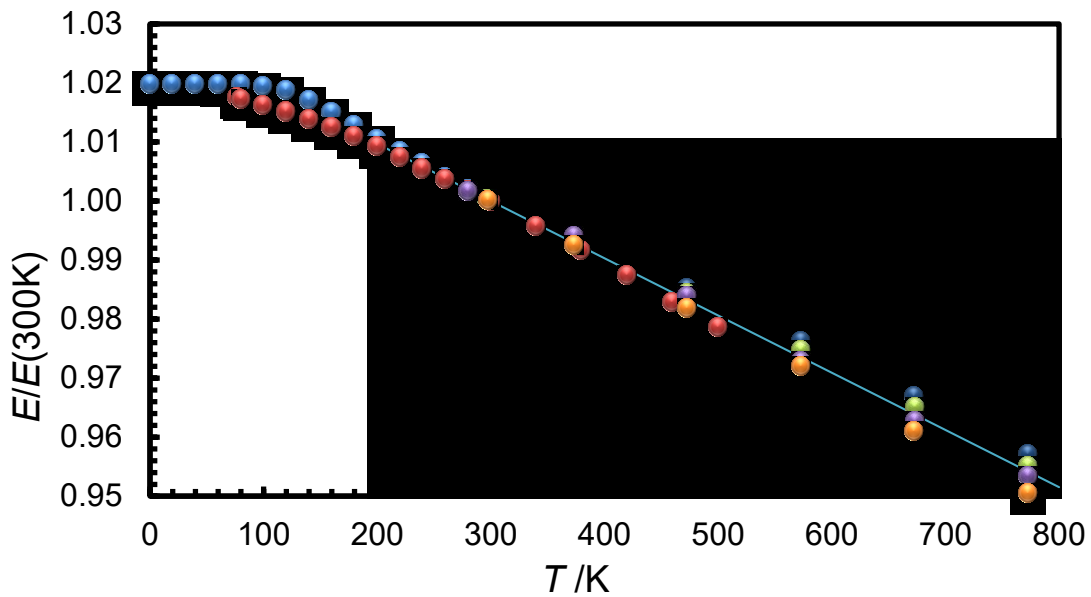


Figure 6.3: Analysis of the elastic-constant data for tungsten, (A) Single crystal tungsten material: ●, Featherston *et al*.[8]; ●, Bolef *et al*.[3]; (B) Polycrystalline tungsten material: ●, Lowrie *et al*.[4]; ●, Bernstein *et al*.[5]; ●, Armstrong *et al*.[6]; and —, Linear function

From Figure 6.3 It was observed that the Young's modulus as reported in these sources was almost the same for materials with similar structure. For instance, the values of E at

300 K for a single crystalline tungsten material as reported by Featherston *et al.*[2]s, Bolef *et al.*[3], and Armstrong *et al.*[6] were 409.8 GPa, 409.4 GPa and 409.0 GPa respectively. Similarly, for polycrystalline tungsten material Lowrie *et al.*[4] and Bernstein *et al.*[5] have reported values of E at 300 K as 401.7 GPa and 403.3 GPa respectively. Furthermore, our analysis also revealed that the difference between the static and dynamic values of E is negligible.

6.5 The sinker properties

For VWVD with suspended sinker, the resonance frequency of the sensor largely depends on the tension on the wire which in-turn, is a function of the sinker properties (i.e. mass and volume). This resonance frequency is related to the density of the fluid surrounding the wire and so, for accurate density determination using this device, the sinker properties need to be accurately determined. In this work, the sinker properties were independently determined by hydrostatic weighing using a precision electronic balance by Mettler Toledo (model PR5003) with a standard uncertainty of 5 mg .

It is important to note that prior to the measurement, the balance was properly cleaned, levelled, auto-calibrated and zeroed. The weighing procedure is described in the following sections.

6.5.1 Mass of the sinker

The Sinker was placed on the digital balance and readings were repeatedly taking from the display and recorded as shown in Table 6.1. The ambient properties i.e. temperature T_a , pressure p_a , and relative humidity RH , were respectively measured as 295.35 K, 101.04 KPa, and 38.4 %.

Table 6.1: Mass of the sinker in ambient air I_a /g and in water I_w /g

	I_a / g	I_w / g
1	403.513	141.584
2	403.514	141.581
3	403.510	141.582
Average	403.512	141.582

the mass recorded was corrected for air buoyancy effects as follows

$$m_c / g = \left[\frac{1 - (\rho_a / \rho_c)}{1 - (\rho_a / \rho)} \right] \times I_a / g, \quad (6.2)$$

where, m_c is the corrected weight of the sinker in g; ρ is the density of the material; ρ_c is the conventional body density, given as 8000 kg/m³; I_a is the weight of the sinker in ambient air as displayed on the balance in g.

ρ_a is the density of air and is given by:

$$\rho_a / (\text{kg} \cdot \text{m}^{-3}) = \frac{0.348444 (p_a / \text{hPa}) - 100 h_a [0.00252 (t_a / ^\circ\text{C}) - 0.020582]}{273.15 + (t_a / ^\circ\text{C})} \quad (6.3)$$

where p_a is the ambient pressure, h_a is the relative atmospheric humidity, and t_a is the ambient Celsius temperature.

Using equations 6.2 and 6.3 above, the true mass of the sinker and the density of air at 295.35 K were calculated as 0.403625 kg and 1.187 kg/m³ respectively.

6.5.2 Volume of the sinker

The volume of the sinker was determined according to an established weighing procedure reported by Moldover, *et al.*[9]. The procedure entails measuring the weight of the sinker in both ambient air and water, and the true density of the sinker was obtained from the following relation:

$$\rho_s / (\text{kg} \cdot \text{m}^{-3}) = [I_a / I_w \cdot (\rho_w - \rho_a) / (\text{kg} \cdot \text{m}^{-3})] + \rho_a / (\text{kg} \cdot \text{m}^{-3}), \quad (6.4)$$

where, ρ_s is the density of the sinker; I_a is the weight of the sinker in ambient air; I_w is the weight of the sinker in water; ρ_w is the density of water at the operating temperature and ρ_a is the density of air at the operating (ambient) temperature

The weight of the sinker in the ambient air was determined as described in the previous section and the corresponding weight in water was determined by filling a cylindrical container to a certain level to which a few drops of non-ionic detergent was added. Prior to the addition of the detergent, the water was properly degassed by placing the cylinder containing the water into an ultrasound bath and allowed to run for about 30 minutes. The cylinder was then placed on the digital balance and the sinker was hung from the top of the balance using a monofilament thread and wholly immersed in the water (as shown in the Figure 6.4, the weight of the sinker in water was then measured and tabulated in Table 6.1.

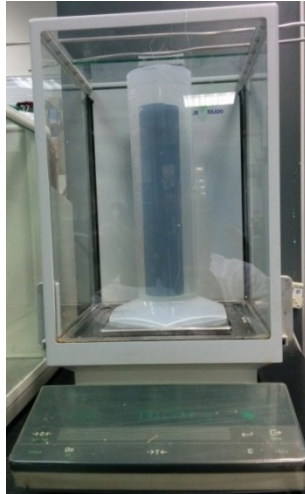


Figure 6.4: Sinkers immersed in water

It is important to note that the sinker was suspended and therefore, not allowed to touch either sides or bottom of the cylinder.

The temperature of the water was measured as 295.35 K using an industrial PRT thermometer immersed in the water and the density of water at this temperature and atmospheric pressure was obtained as 997.720 kg/m³ from IAPWS 1995 formulation by Wagner and Pruss[10] available in NIST database.

The density of the sinker was obtained from equation 6.4 and then the volume of the sinker was calculated using the following relation

$$V_s / \text{m}^3 = \frac{m_c / \text{kg}}{\rho_s / (\text{kg} \cdot \text{m}^{-3})} \quad (6.5)$$

where; V_s , m_c and ρ_s are the volume, mass and density of the sinker respectively

The properties of the sinker are summarised in the Table 6.2 below

Table 6.2: Measured sinker properties

T_w / K	293.35
$\rho_a / (\text{kg} \cdot \text{m}^{-3})$	1.187
m_c / kg	0.404
$\rho_s / (\text{kg} \cdot \text{m}^{-3})$	2841.324
V_s / m^3	0.142

$$U(m_c) = \pm 0.1 \text{ mg} \text{ and } u(V_s) = \pm 0.06 \text{ cm}^3$$

6.6 Vacuum properties

The vacuum resonance frequency and the vacuum logarithmic decrement are also important parameters in the governing equation of VW device. For convenience, both parameters were determined by conducting several scans in nitrogen at atmospheric pressure over the entire operating temperature range in this work. The measured properties were converted to their corresponding vacuum equivalent and then adjusted by minimising the sum of the square difference of these values and those calculated from equations. The calculated resonance frequency is related to the sinker and the wire properties discussed above and it is obtained from equation 3.58 in section 3.4 re-written as follows.

$$f_0 = \sqrt{\frac{(m_s - \rho V_s)g}{4L^2 \rho_w \pi R^2}} + \sqrt{\frac{ER^2}{4\rho_w L^4}} + \frac{1}{2L} \left(4 + \frac{\pi^2}{2} \right) \sqrt{\frac{E^2 \pi R^6}{16(m_s - \rho V_s) \rho_w g L^4}} \quad (6.6)$$

where, m_s , V_s and ρ are the mass, volume and density of the sinker respectively and, R , L , ρ_w and E are respectively the radius, length, density and the young modulus of the wire

It was found that for a centreless-ground tungsten wire with properties (i.e. radius and length) as described in the previous section and tensioned by an aluminium sinker having properties (i.e. m_s , V_s , ρ_s) as presented in Table 6.2 would have a resonance frequency of about 871 Hz in nitrogen at ambient condition.

Similarly, the logarithmic decrement of the wire in vacuum is related to the corresponding decrement in nitrogen via the following relation.

$$\Delta_0 = \left(\Delta'_0 - \frac{1}{2} \beta' \right) \quad (6.7)$$

where Δ_0 is the true logarithmic decrement in vacuum and calculated as 22.6 μ , Δ'_0 is the measured decrement of the wire in nitrogen, β' is the added damping parameter for nitrogen and the density of nitrogen was taken from equation of state by Span *et al.*[11] and the viscosity from Lemmon and Jacobsen[12] both available in NIST reference database. Figure 6.5a shows that the resonance frequency decreases linearly with increase in temperature, and (b) shows how the decrement in nitrogen fluctuates with increase in temperature.

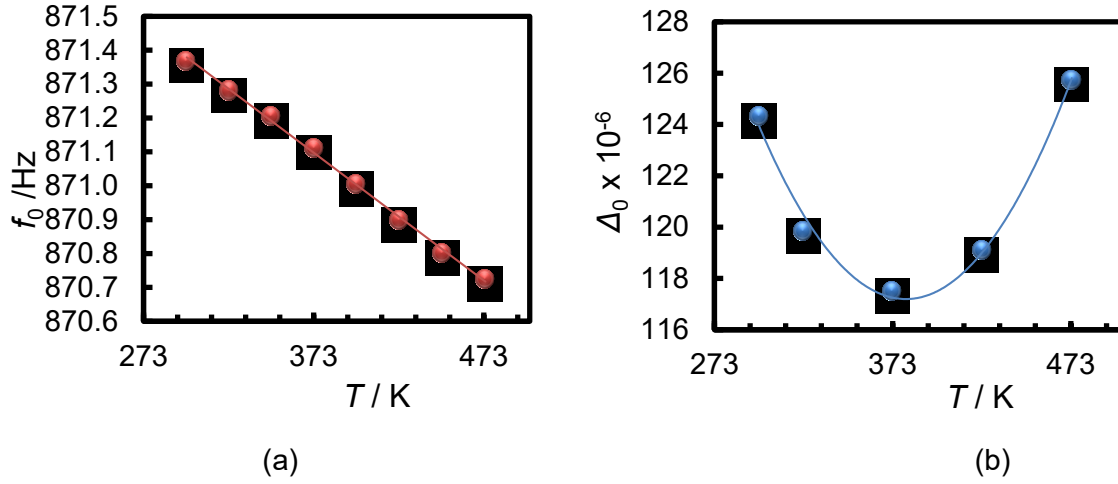


Figure 6.5(a). Dependence of both resonance frequency f_0 /Hz and, (b) logarithmic decrement Δ_0 on temperature T /K

6.7 The vibrating u-tube densimeter VTD

The vibrating u-tube densimeter in the 1 kbar set-up was calibrated in fluids of widely known properties to determine two key parameters A and B in the working equation of the VTD device. However, unlike the vibrating-wire, the densimeter is calibrated by measuring the periods of oscillations of the vibrating tube over the full temperature and pressure operating limits using at least two fluids. The calibration fluids are normally chosen from the low-density fluid and a fluid with similar density (high density) as the intended fluid to be measured. However, as it is difficult to find two fluids with widely known density over the desired temperature and pressure range in the literature, Lagourette *et al.*[13] and Sousa *et al.*[14] proposed eliminating the second calibration fluid and instead suggested determining the period of oscillation of the vibrating tube under vacuum. In this work, the VTD was calibrated three times and in the first calibration, de-ionized water, and vacuum were used and a large body of data was obtained and regressed to obtain the two parameters described as

$$\rho(p, T) = A(p, T)\tau^2 - B(p, T), \quad (6.8)$$

where ρ is the density of the fluid in the tube; A and B are physical constants both functions of temperature and pressure and τ is the period of oscillation of the tube. In equation 6.8, it was assumed that both parameters have a linear dependence on pressure and cubic dependence on temperature as shown in equations below

$$A(p, T) = \sum_{i=0}^1 \sum_{j=0}^3 a_{i,j} (p/\text{MPa})^i (T/\text{K})^j, \quad (6.9)$$

$$B(p, T) = \sum_{i=0}^1 \sum_{j=0}^3 a_{i,j} (p/\text{MPa})^i (T/\text{K})^j. \quad (6.10)$$

The coefficients of equations 6.9 and 6.10 were obtained by regression analysis and a total of 16 parameters were recorded in Table 6.4. Figure 6.6 presents the deviation plot from the first calibration.

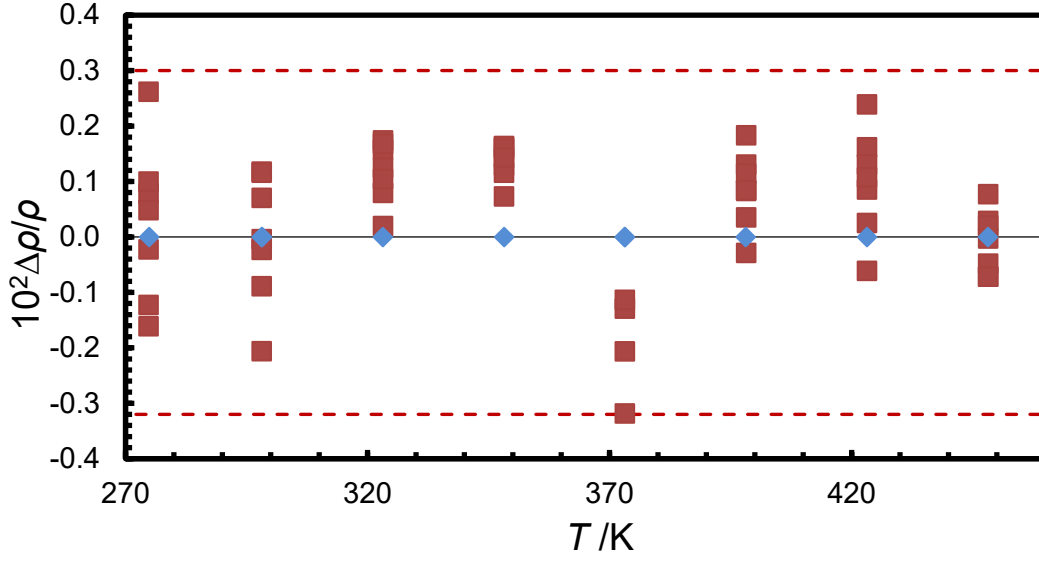


Figure 6.6: Deviations of the calculated density of the first VTD calibration data from equation 6.8 against temperature T : $\blacklozenge$, Vacuum data and $\blacksquare$ De-ionized water data

Following the first calibration, it was observed that the deviations from the de-ionized water data were larger than what was expected and so, we repeated the same procedure and added toluene as a third calibration fluid. The density of toluene were taken from the reference equation of state of Lemmon E.W and Span R.[15] available in NIST database. Figure 6.7 shows the density deviations from the results of the second calibrations.

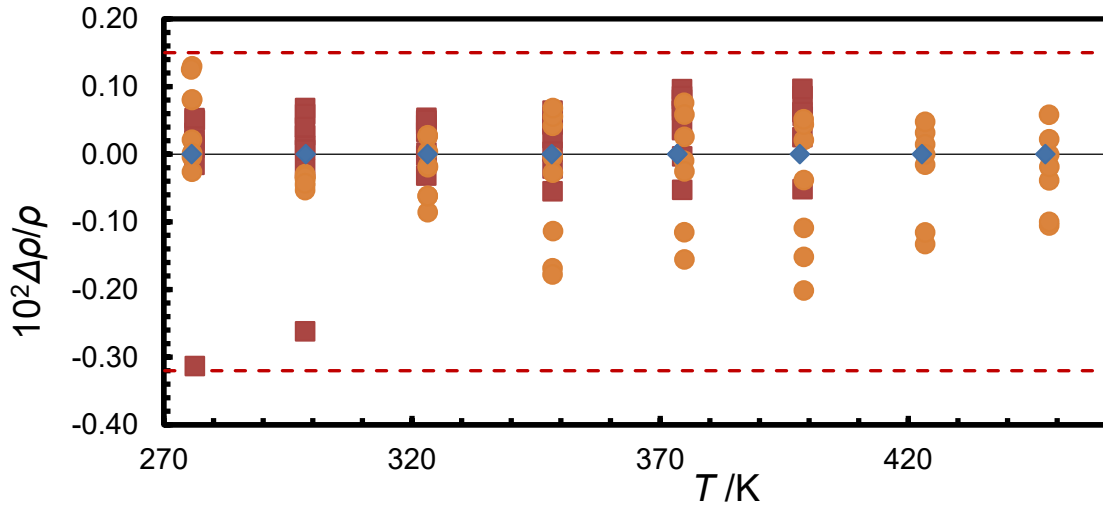


Figure 6.7: Deviations of the calculated density of the second VTD calibration data from equation 6.8 against temperature T : $\blacklozenge$, Vacuum data and $\blacksquare$ De-ionized water data and $\bullet$, Toluene data

Although, slight improvement was observed as the deviations from the second calibration data were smaller than those from the first calibration and the deviations from the toluene data are even smaller than those of the de-ionized data. However, looking at Figure 6.7 the deviations in density are still larger than the overall expanded uncertainty of the VTD device of 0.2 % and so it was decided to identify the possible sources of error in the system. After thorough investigation, it was found that the insulations around the VTD as well as the flow lines were not adequate as such there might be heat some heat loses in the VTD. Having identified this, the insulations around the VTD was improved and those on the flow lines were replaced as shown in Figure 5.12.

Following the improvement in the insulations, additional vacuum calibration was conducted and the results was fitted as a quadratic functions of temperature described by the equation below and compared with the corresponding values from the second calibration as shown in Figure 6.8.

$$\tau_{\text{vac.}} / \mu\text{s} = \sum_{i=0}^2 k_i (T / \text{K})^i \quad (6.11)$$

Table 6.3: Coefficients of equation 6.11

Coefficients	2 nd Cal.	3 rd Cal.
k_0	2.47E+03	2.47E+03
k_1	9.70E+00	9.90E+00
k_2	6.94E+01	6.87E+01

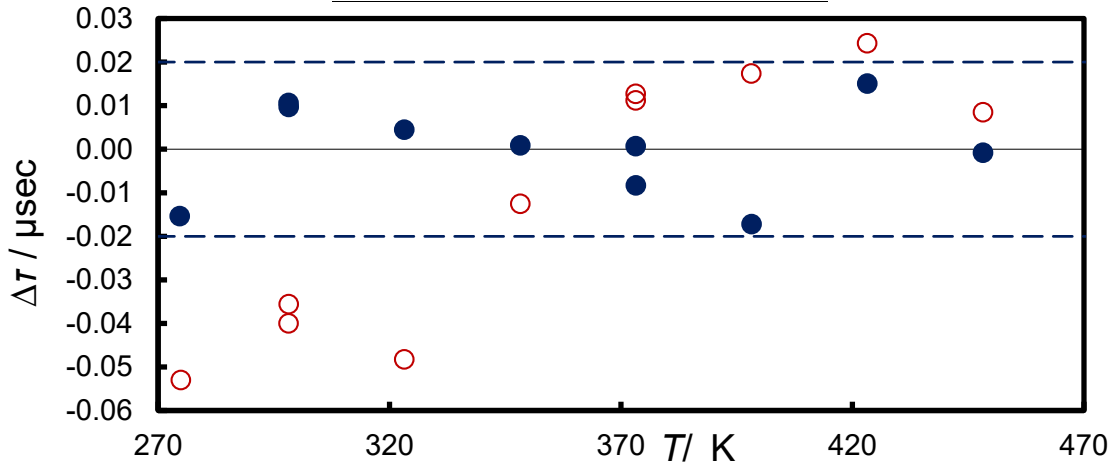


Figure 6.8: Comparisons of the vacuum period of oscillations of the second and third calibrations with equation 6.8 against temperature T . $\circ$, Second calibration and $\bullet$, third calibration

The difference in the vacuum period of oscillations observed in Figure 6.9 justified our claim on the insulation and also prompted decision to repeat the water and toluene

calibrations for the third time. Figure 6.9 illustrates the comparison of the de-ionized water and toluene data for the second and third calibrations.

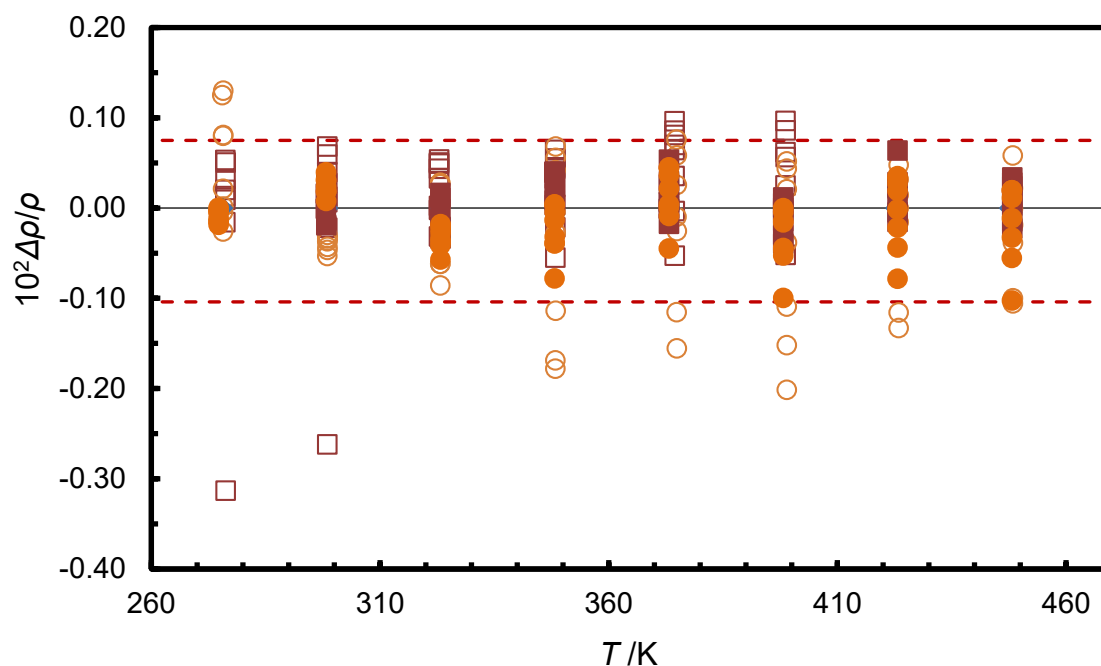


Figure 6.9: Comparison of both de-ionized water and toluene data of the second and third calibrations with equation 6.8 against temperature: open symbols represent the results of the second calibration and the filled symbols represent the results of the third calibration. $\square$, D.I water data and $\bullet$, Toluene data

From Figure 6.9, it can be observed that the results of the third calibration present smaller deviations which contained within ± 0.1 % for both de-ionized water and toluene data and which is good enough to give the overall expanded uncertainty of 0.2 % of the VTD and hence, the densimeter calibration was successful.

Table 6.4: Coefficients of equation 6.1 for the 1st, 2nd and 3rd calibration of the VTD

coefficients	1 st Cal.	2 nd Cal.	3 rd Cal.
a_{00}	1.92E+04	2.00E+04	1.83E+04
a_{01}	-4.12E+03	-7.14E+03	-1.86E+03
a_{02}	1.96E+03	5.35E+03	2.15E+02
a_{03}	-4.68E+02	-1.63E+03	-3.39E+01
a_{10}	8.77E+01	-2.32E+02	-2.77E+01
a_{11}	-1.86E+02	4.94E+02	5.46E+01
a_{12}	1.20E+02	-3.54E+02	-3.76E+01
a_{13}	-2.47E+01	8.29E+01	8.62E+00
b_{00}	1.81E+04	1.91E+04	1.71E+04
b_{01}	-3.08E+03	-6.36E+03	-6.10E+02
b_{02}	2.16E+03	5.76E+03	2.06E+02
b_{03}	-5.05E+02	-1.73E+03	-1.47E+01
b_{10}	9.12E+01	-2.42E+02	-2.86E+01
b_{11}	-1.91E+02	5.13E+02	5.64E+01
b_{12}	1.22E+02	-3.66E+02	-3.87E+01
b_{13}	-2.45E+01	8.50E+01	8.83E+00
$10^2\Delta_{\text{MAD},\rho}$	0.29	0.26	0.10
$10^2\Delta_{\text{AAD},\rho}$	0.07	0.09	0.02
$10^2\Delta_{\text{Bias},\rho}$	0.00	-0.01	0.00

6.8 Measurement procedure

After cleaning the system, the pure liquid sample was degassed under vacuum and constant stirring. A known amount of pure liquid sample was then injected to fill the system excluding the accumulator. The manual screw injector in the fluid handling system was used to withdraw additional liquid (when necessary) and also to raise pressure in the system. The desired condition of temperature and pressure was then set and allowed to equilibrate before measurement on pure liquid sample was commenced.

The VWVD equipment set-up shown in Figure 5.1 allows the study of mixtures of liquid with dissolved gases. One of the advantages of this configuration is that, mixtures of gas and liquid could be prepared *in situ* with the aid of the accumulator (PulseGuard Ltd, Model PiG-SS) thereby avoiding the difficulty and danger of transferring mixtures under high pressure. To prepare a mixture of liquid and gas of known composition, a predetermined amount of liquid was first injected into the system with the accumulator isolated from the loop. The accumulator's inlet valve was then gently cracked to bleed

some liquid into it thereby creating space in the system for the addition of gas component. The gas supply was then connected to the inlet line and gas admitted thereby pushing the liquid in the inlet lines into the system. The amount of gas transferred into the system was monitored approximately by continuous weighing of the cylinder, and the final amount of gas injected was determined by additional weighing of the uncoupled cylinder on a precision balance described in the previous section.

After the injection of the required amount of liquid and gas into the system, the pressure of the system was then raised to slightly above the saturation pressure of the mixture. The circulation pump in the fluid handling system was then actuated and allowed to run continuously for about 7 to 10 hours after which the mixture was brought to a single homogenous liquid phase. After homogenising the mixture, the pressure was adjusted to the desired value and measurement was conducted along isotherms from (0.1 to 200) MPa at the desired pressure intervals. When measurements are completed on a given isotherm, the lowest pressure was always repeated to check for repeatability and any apparent solvent degradation that might occur during the measurement circle.

6.9 Validation measurements

Following the implementation of several modifications on the VWVD apparatus and due to the fact that there was not any rigorous calibration conducted on the device, it was necessary to test and validate the apparatus by comparing our measurements with some reference standards. The validation measurements were conducted on liquid viscosity standard S20 (obtained from Paragon Scientific Ltd.) at atmospheric pressure in the temperature range (298.15 to 373.26) K. The viscosity and density values obtained from the VWVD measurements were compared with the values on the datasheet supplied by the Paragon Scientific Ltd. A Very good agreement was observed in both viscosity and density values obtained by VWVD and the calibration datasheet. Figures 6.10 and 6.11 show the comparisons between the VWVD results and values from the supplied datasheet from Paragon scientific for density and viscosity respectively. Deviation plots for both density and viscosity were plotted and it is evident from Figure 6.10 that the density deviations were generally less than the 0.2 % overall uncertainty of the VWVD device. Similarly, it can be seen from Figure 6.11 that the viscosity deviations are within the expected uncertainty of 2 % of the VWVD apparatus.

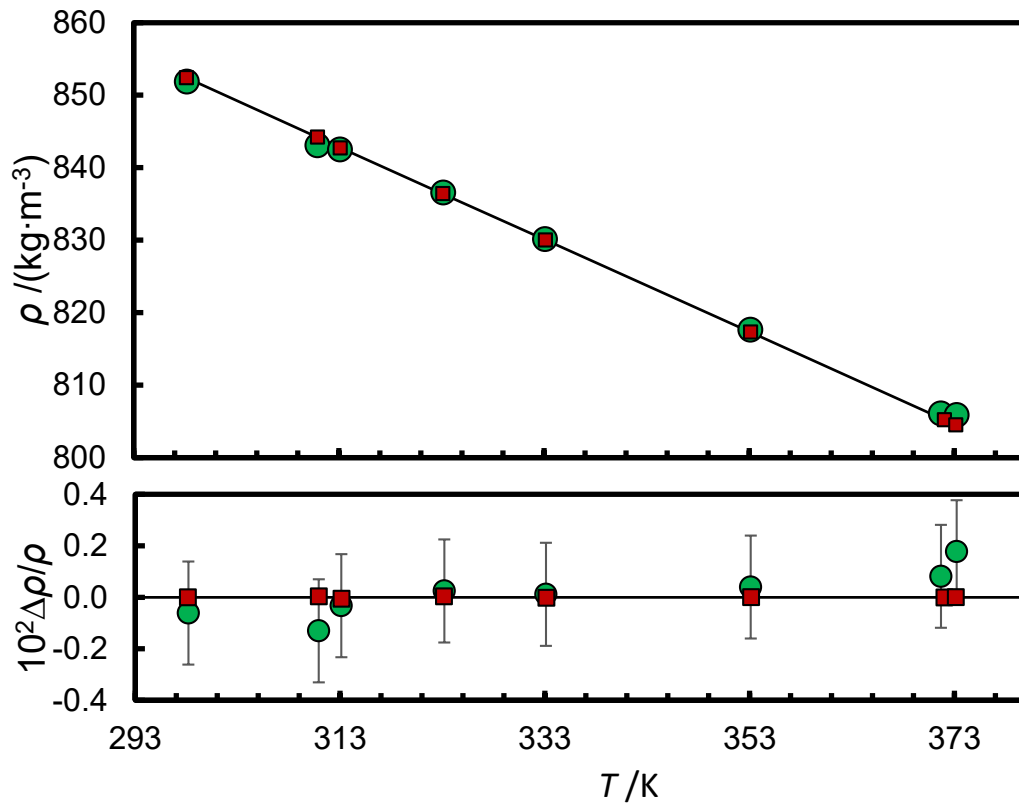


Figure 6.10: Comparison of the experimental density of S20 viscosity standard against the calibration data supplied by Paragon Scientific Ltd. ●, VWVD measurements and ■, Paragon data

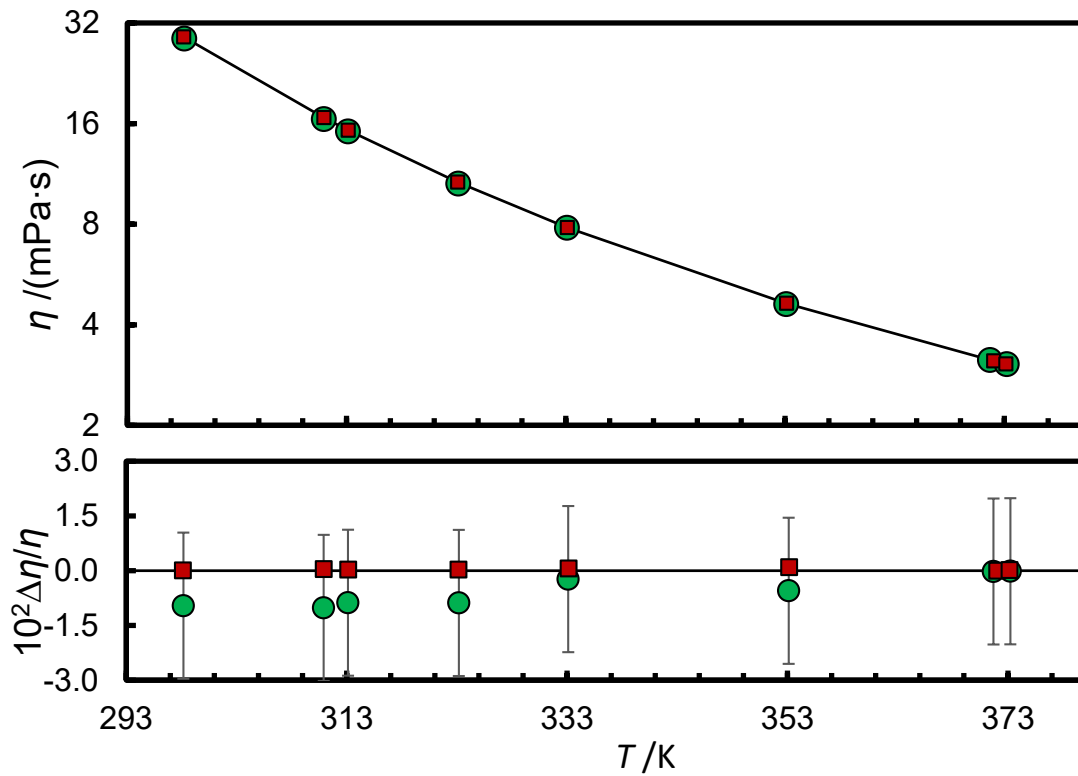


Figure 6.11: Comparison of the experimental viscosity of S20 viscosity standard against the calibration data supplied by Paragon Scientific Ltd. ●, VWVD measurements and ■, Paragon data

These results gave us the confidence to proceed with measurements on other samples of interest and hence the device was validated and recommisioned.

Table 6.5: Statistical parameters for density of S20

	Calibration data	VWVD data
$10^2 \Delta_{AAD,\rho}$	0.00	0.07
$10^2 \Delta_{MAD,\rho}$	0.01	0.18
$10^2 \Delta_{bias,\rho}$	0.00	0.01

Table 0.1: Statistical parameters for viscosity of S20

	Calibration data	VWVD data
$10^2 \Delta_{AAD,\eta}$	0.04	0.37
$10^2 \Delta_{MAD,\eta}$	0.10	1.02
$10^2 \Delta_{bias,\eta}$	0.00	-0.57

6.10 Uncertainty analysis

There are numerous possible sources of error in measuring the viscosity of a given fluid. Some of these sources of error could be attributed to poor design of the apparatus, whereas others could result from the experimental methodology. Although, it is important to identify and eliminate all potential sources of error where possible, however, some of these errors can only be minimised and, as such could lead to some systematic deviations from the normal expected behaviour. In this situation, it is imperative to properly determine and quantify the impact of these errors in order to get good understanding of the data produced and, for comparing with other literature data available. The following section, highlights some of the potential sources of error in viscosity measurements using the vibrating wire device and how to minimise them.

6.10.1 Control of various sources of error

Most of the potential sources of error in viscosity measurement can be minimized or eliminated in the following ways^[16]:

- Appropriate instrument design or selection of suitable component,
- Avoiding excessive noise levels
- Avoiding cross-contamination of the samples
- Steady state conditions

- Accurate calibration/determination of measured quantities in the working equations

Too much assumptions and over-simplification in the instrument design could lead to departure from the governing theory and can lead to considerable systematic error in measurements. In the vibrating wire viscometer, the major sources of error are the boundary effects and over-excitation of the wire. To overcome this, Retsina *et al.*^[17, 18] and Assael *et al.*^[19] indicated that making the radius of the container/vessel 80 time larger than that of the wire, the systematic error in neglecting the outer boundary condition is of the order 0.05 % in viscosity. In this experiment, the ration of the radius of the container to that of the wire was in the excess of 200 and hence, error due to boundary condition is negligible. To overcome the over-excitation problem, we make sure as a rule of thumb that the amplitude of the resonance peak was always kept in the range ($40 < V/\mu V < 150$) by using a drive voltage that ensured an offset baseline of 0 volt could be achieved when far away from the resonance. This would prevent over-running the wire and also would ensure that error in viscosity due to the over excitation of the wire was minimise and kept in the order of 0.1 %. Furthermore, the background noise was minimised by scanning the resonance frequency width at least twice, in upward and reverse directions in equal frequency interval of 0.1 Hz. By this approach, two sets of data were obtained at each point and, the average was used in the fit, thereby reducing the noise level and minimising the uncertainty in the resonance frequency significantly^[20].

Cross-contamination of samples with any previously used solvent was avavoided by following a comprehensive cleaning protocol of the VWVD device as outlined in section 6.1. Furthermore, when draining the system, the fluid coming from the outlet valve is visually monitored for any obvious change in coluor due to corrosion or any other cause. In addtion, repeat measurements were conducted at the lowest pressure at the end of each isotherm cycle. This was to check if there is any change in the properties of the fluid and/or the device settings has been compromised during the experiment. In any case, the repeatability of the check measurements has to be within ± 0.5 % in viscosity and ± 0.1 % in density from the initial measurements before the value is recorded and, if the difference is in excess of ± 1 % maximum tolerance, then the sample was discarded and experiment repeated with a new sample. More so, impurities if not having similar properties (such as boiling point) as the sample can lead to some errors in the experiment. For this reason, a GC-MS analysis was employed to characterise the impurities and also to determine their relative proportion in the pure sample. In all the systems investigated in this research, it was found that the percentage of the dominant impurities were less than 0.1 % and also they have similar properties as the pure samples, thus their effects on viscosity and density were negligible.

6.10.2 Repeatability and overall uncertainty calculations

The repeatability has been investigated by analysing large body of datasets from simultaneous viscosity and density measurements on krytox[®] oil and those from pure hexadecane and its binary mixtures with methane, all measured in this work. These datasets cover wide range of density and viscosity of (645 to 875) kg·m⁻³ and (0.268 to 5.080) mPa·s for hexadecane and its mixtures; (1514 to 1700) kg·m⁻³ and (1.132 to 97.22) mPa·s. for krytox[®] oil respectively. Furthermore, the analysis was conducted for the full temperature and pressure operating limits of the device. Figure 6.12(a) presents the repeatability in density whereas Figure 6.12(b) shows the average viscosity repeatability from three consecutive repeated measurements at each data point for the two data sets.

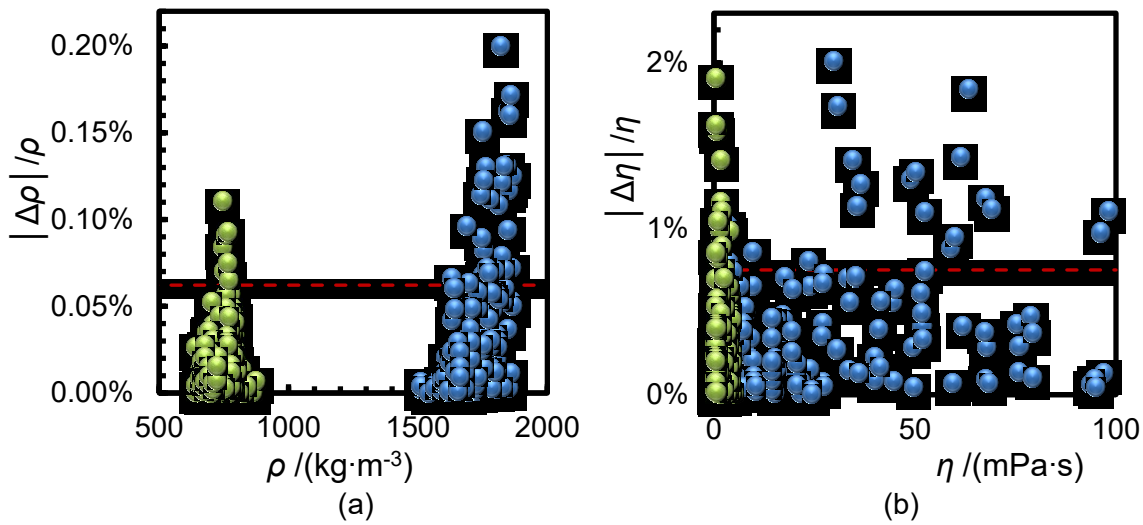


Figure 6.12: Absolute differences of the experimental data from their respective mean values of three consecutive repeated measurements at each data point (a) density and (b) viscosity. ●, hexadecane and its binary mixtures data; ●, krytox[®] data and — — —, 95 % confidence level

From Figure 6.12, it can be seen that more than 95 % of both datasets are repeatable to within 0.1 % in density and to less than 0.7 % in viscosity. In addition, the remaining of the data are mostly from the krytox[®] data due to its high density. Furthermore, the density and viscosity deviations from their respective mean values of three consecutive repeated measurements at each data point were illustrated in Figure 6.13.

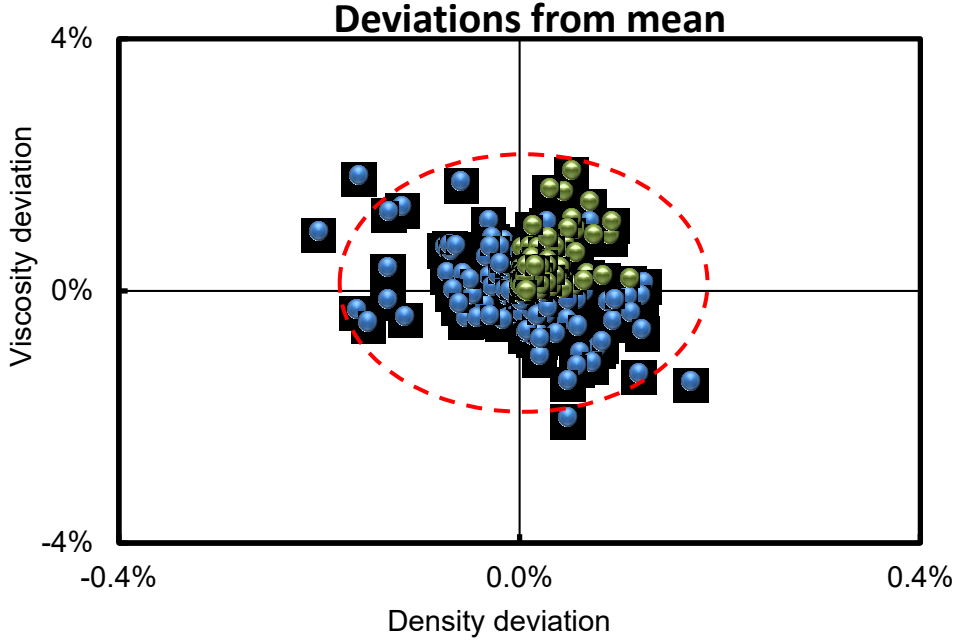


Figure 6.13: Viscosity and density deviations from the mean values of three consecutive repeated measurements at each point. ●, hexadecane and its binary mixtures data; ●, krytox® data.

Although, there is not any evidence to suggest that increase in density deviations can lead to corresponding increase in the viscosity deviations from Figure 6.13, however, we note that the two quantities are highly correlated in the resonance frequency model in the governing equation of the device.

6.10.3 Uncertainty of measured quantities

The vibrating wire employed in this work was operated in absolute mode with no any prior rigorous calibration of the device. In this approach, the key parameters in the governing equations were independently determined from mechanical measurements. Therefore, the uncertainties in these individual measurements would contribute to the overall uncertainty of the experiment. The overall uncertainties in both density and viscosity are computed following the guide to the expression of uncertainty in measurements (GUM)[21], and the detailed analysis will be presented in[22]. In this approach, the overall uncertainty in any measured property is determined from the standard uncertainties and partial derivatives of set of quantities that serve to determine the property, as given by

$$u_r^2(Y) = \sum_i \left[\left(\frac{\partial \ln Y}{\partial \ln z_i} \right)_{z_j \neq i} u_r(z_i) \right]^2, \quad (6.12)$$

where, Y represent a dependent measured property (e.g. viscosity or density) and z_i ($i = 1, 2, 3 \dots$) are the set of experimental quantities that serve to determine Y .

For density, in order to determine the partial differentials with respect to the experimental quantities other than temperature and pressure, the density was derived from equation 3.58 and after making some simplifications can be expressed in analytical form as

$$\rho = \frac{(m/V)(1-X^2)}{1+X^2(m/V)\rho_w^{-1}k_{\text{res}}}, \quad (6.13)$$

where X is given as

$$X = \frac{f_{\text{res}} - f_1}{f_{0,\text{vac}} - f_1} \quad (6.14)$$

From equations 6.13 and 6.14, the measured quantities that determine the density are: m and V for mass and volume of the sinker; and the frequency terms; f_{res} , f_1 and $f_{0,\text{vac}}$. The differential coefficients of density with respect to these terms are summarised in Table 6.6.

Table 6.6: Differential coefficients required for the analysis of the uncertainties in the density

$\left(\frac{\partial \ln \rho}{\partial \ln m}\right) = \frac{1}{1+F_0}$	$\left(\frac{\partial \ln \rho}{\partial \ln R}\right) = -F_1 F_2 f_1$
$\left(\frac{\partial \ln \rho}{\partial \ln V}\right) = \frac{-1}{1+F_0}$	$\left(\frac{\partial \ln \rho}{\partial \ln L}\right) = 2F_1 F_2 f_1$
$\left(\frac{\partial \ln \rho}{\partial \ln f_{0,\text{vac}}}\right) = F_1 \left(\frac{f_{0,\text{vac}}}{f_{0,\text{vac}} - f_1}\right)$	$\left(\frac{\partial \ln \rho}{\partial \ln E}\right) = \frac{-F_1 F_2 f_1}{2}$
$\left(\frac{\partial \ln \rho}{\partial \ln f_{\text{res}}}\right) = -F_1 \left(\frac{f_{\text{res}}}{f_{\text{res}} - f_1}\right)$	$\left(\frac{\partial \ln \rho}{\partial \ln \rho_w}\right) = \frac{F_1 F_2 f_1}{2} + \frac{F_0}{1+F_0}$
$\left(\frac{\partial \ln \rho}{\partial \ln \Omega_{\text{res}}}\right) = \left(\frac{-F_0}{1+F_0}\right) \left(\frac{\partial \ln k}{\partial \ln \Omega}\right)_{f=f_{\text{res}}}$	$F_1 = \frac{2X^2}{1-X^2} + \frac{2F_0}{1+F_0}$
$F_0 = X^2(m/V)\rho_w^{-1}k_{\text{res}}$	$F_2 = \left(\frac{1}{f_{0,\text{vac}} - f_1} - \frac{1}{f_{\text{res}} - f_1}\right)$

For the viscosity, equation 3.6 evaluated at $f = f_{\text{res}}$ and can be re-written in the following form;

$$\eta = \frac{2\pi f_{\text{res}} \rho R^2}{\Omega_{\text{res}}}. \quad (6.15)$$

From equation 6.15, the quantities that determine the viscosity are (f_{res} , ρ , R and Ω_{res}) and it can be seen this that the uncertainty in viscosity is dominated by the uncertainty in determining the radius of the wire. From equation 6.15, the coefficients of the differentials of viscosity with respect to these quantities are described in Table 6.7.

Table 6.7: Differential coefficients required for the analysis of the viscosity

$\left(\frac{\partial \ln \eta}{\partial \ln R}\right) = 2$	$\left(\frac{\partial \ln \eta}{\partial \ln \rho}\right) = 1 + \left(\frac{\partial \ln k'}{\partial \ln \Omega}\right)_{f=f_{\text{res}}}^{-1}$
$\left(\frac{\partial \ln \eta}{\partial \ln f_{\text{res}}}\right) = 1$	$\left(\frac{\partial \ln \eta}{\partial \ln \Omega_{\text{res}}}\right) = -1$
$\left(\frac{\partial \ln \eta}{\partial \ln \rho_w}\right) = -\left(\frac{\partial \ln k'}{\partial \ln \Omega}\right)_{f=f_{\text{res}}}^{-1}$	$\left(\frac{\partial \ln \eta}{\partial \ln \Delta_0}\right) = \frac{2\Delta_0 \rho_w}{k'_{\text{res}} \rho} \left(\frac{\partial \ln k'}{\partial \ln \Omega}\right)_{f=f_{\text{res}}}^{-1}$

6.10.4 Uncertainties of the wire and sinker properties

As mentioned earlier, both radius and length of the wire were obtained from direct independent measurements. The standard uncertainties in determining radius and length of the wire at reference conditions were 0.1 μm and 0.01 mm respectively. Both quantities are calculated at other temperatures and pressures using the following equation.

$$\left. \begin{aligned} \ln(R/R_0) &= \alpha_w(T - T_0) - \frac{1}{3}\beta_w(p - p_0) \\ \ln(L/L_0) &= \alpha_w(T - T_0) - \frac{1}{3}\beta_w(p - p_0) \end{aligned} \right\} \quad (6.16)$$

the density of the wire was obtained from the literature, as reported by Parrish *et al.*[1] as $\rho = 19254 \text{ (kg}\cdot\text{m}^{-3}\text{)}$ at 298.15 K and values at other temperatures are obtained as follows;

$$\ln(\rho_w/\rho_{0,w}) = -3\alpha_w(T - T_0) + \beta_w(p - p_0) \quad (6.17)$$

In equation 6.6 α_w is the linear thermal expansion coefficient and β_w isothermal the compressibility of tungsten wire and both quantities were taken from the literature. The relative uncertainty of α_w affects that ρ through the partial derivative:

$$\left(\frac{\partial \ln \rho}{\partial \ln \alpha_w}\right) = \left[\left(\frac{\partial \ln \rho}{\partial \ln R}\right) + \left(\frac{\partial \ln \rho}{\partial \ln L}\right) - 3\left(\frac{\partial \ln \rho}{\partial \ln \rho_w}\right)\right] \alpha_w(T - T_0) \quad (6.18)$$

and the viscosity through

$$\left(\frac{\partial \ln \eta}{\partial \ln \alpha_w} \right) = \left(\frac{\partial \ln \eta}{\partial \ln R} \right) \alpha_w (T - T_0) \quad (6.19)$$

In a similar way, the relative uncertainty in β_w influences the uncertainties of both density and viscosity in the following ways;

density;

$$\left(\frac{\partial \ln \rho}{\partial \ln \beta_w} \right) = \left[- \left(\frac{\partial \ln \rho}{\partial \ln R} \right) - \left(\frac{\partial \ln \rho}{\partial \ln L} \right) + 3 \left(\frac{\partial \ln \rho}{\partial \ln \rho_w} \right) \right] \beta_w (p - p_0) \quad (6.20)$$

and viscosity;

$$\left(\frac{\partial \ln \eta}{\partial \ln \beta_w} \right) = - \left(\frac{\partial \ln \eta}{\partial \ln R} \right) \beta_w (p - p_0) \quad (6.21)$$

The Young's modulus of the wire can be expressed as a function of temperature as follows;

$$\ln(E/E_0) = \varepsilon_w (T - T_0) \quad (6.22)$$

where, ε_w is the temperature dependent coefficient of E and $E_0 = E(T_0)$. The uncertainties in determining ε_w influences ρ through;

$$\left(\frac{\partial \ln \rho}{\partial \ln \varepsilon_w} \right) = \left(\frac{\partial \ln \rho}{\partial \ln E} \right) \varepsilon_w (T - T_0) \quad (6.23)$$

The volume of the sinker at reference temperature and pressure was determined by hydrostatic weighing via equation 6.5 re-written in the following form;

$$V_0 = m \left[(l_{\text{air}} / l_{\text{water}}) (\rho_{\text{water}} - \rho_{\text{air}}) + \rho_{\text{air}} \right]^{-1} \quad (6.24)$$

here m is the true mass of the sinker, and l_{air} and l_{water} are the apparent masses measured in air (of density ρ_{air}) and water (of density ρ_{water}), respectively. From this equation, it follows that the standard relative uncertainty of V_0 is

$$u_r^2(V_0) \approx u_r^2(m) + u_r^2(l_{\text{air}}) + u_r^2(l_{\text{water}}) + u_r^2(\rho_{\text{water}}) \quad (6.25)$$

$u_r(m) \approx u_r(l_{\text{air}})$, and, for practical purposes, $u_r(\rho_{\text{water}}) = (\partial \ln \rho_{\text{water}} / \partial T)_p u(T_{\text{water}})$, where the standard uncertainty of the measured water temperature, $u(T_{\text{water}}) = 0.1$ K. The values of l_{air} and l_{water} are determined as per Table 6.1 and the relative uncertainties of $u_r(l_{\text{air}}) = u_r(l_{\text{water}}) = 1.5 \times 10^{-6}$ kg. The sinker volume at other temperatures are calculated from;

$$\ln(V/V_0) = 3\alpha_s(T - T_0) - \beta_s(p - p_0) \quad (6.26)$$

where α_s is the linear thermal expansion coefficient and β_s is the isothermal compressibility of the sinker, which were taken from the literature and assumed to be independent of T and p . The uncertainty of the sinker volume is coupled to the uncertainty of density only and the relevant partial derivatives are

$$\left(\frac{\partial \ln \rho}{\partial \ln \alpha_s} \right) = 3 \left(\frac{\partial \ln \rho}{\partial \ln V} \right) \alpha_s (T - T_0), \quad (6.27)$$

and

$$\left(\frac{\partial \ln \rho}{\partial \ln \beta_s} \right) = - \left(\frac{\partial \ln \rho}{\partial \ln V} \right) \beta_s (p - p_0). \quad (6.28)$$

The values, source and uncertainties of the coefficients α_w , α_s , β_w , β_s and ε_w are detailed in Table 6.9. The uncertainties were estimated based on the variability of the literature data. Based on the reported values of E_0 in the literature (shown in Figure 6.8) for different tungsten material, we note that the values of E_0 were known with sufficient accuracy and therefore, only the value of A was adjusted to best fit the measured vacuum resonance frequency. We ascribe to E_0 a standard uncertainty of 10 GPa⁻¹ based on differences between the fitted value and data from different literature sources as shown in Figure 6.8.

Table 6.8: Differential properties of the wire and the sinker material

Dimensionless quantity	z	$u(z)$	$10^2 u_r(z)$	Source
α_w/K^{-1}	4.5×10^{-6}	0.32×10^{-6}	7.0	[23]
β_w/MPa^{-1}	3.24×10^{-6}	0.03×10^{-6}	1.0	[2-5]
ε_w/K^{-1}	-9.7×10^{-5}	0.2×10^{-5}	5.0	This work
α_s/K^{-1}	23.6×10^{-6}	0.7×10^{-6}	3.0	[24]
β_s/MPa^{-1}	14.3×10^{-6}	0.7×10^{-6}	5.0	

6.10.5 Temperature and pressure uncertainties

To obtain the partial differentials of both viscosity and density with respect to temperature and pressure, the correlating equations developed in work were used. The density was correlated using the modified Tait equation and the partial derivatives with respect to temperature and is given as.

$$\left(\frac{\partial \ln \rho}{\partial \ln T}\right)_p = \left(\frac{d \ln \rho_0}{d \ln T}\right) - \left(\frac{\rho}{\rho_0}\right) T \left(\frac{dB}{dT}\right) \left[\frac{C(p-p_0)}{(p_0+B)(p+B)}\right] \quad (6.29)$$

and,

$$\left(\frac{\partial \ln \rho}{\partial \ln p}\right)_T = \left(\frac{Cp}{p+B}\right) \left(\frac{\rho}{\rho_0}\right) \quad (6.30)$$

The viscosity was correlated using the Tait-Andrade equation and the derivatives with respect to temperature and pressure given by

$$\left(\frac{\partial \ln \eta}{\partial \ln T}\right)_p = \frac{-TB_\eta}{(T+C_\eta)^2} + T \left(\frac{dD}{dT}\right) \ln \left(\frac{p+E}{p_0+E}\right) - T \left(\frac{dE}{dT}\right) \left[\frac{D(p-p_0)}{(p_0+E)(p+E)}\right] \quad (6.31)$$

and,

$$\left(\frac{\partial \ln \eta}{\partial \ln p}\right)_T = \frac{Dp}{p+E} \quad (6.32)$$

In equations (6.17 to 6.20), ρ_0 , B and D are quadratic functions of temperature while E is a quadratic function of inverse of temperature as shown in equations (7.2, 7.3, 7.8 and 7.9) and their derivatives with respect to temperature are given as

$$\left. \begin{aligned} \frac{\partial \rho_0}{\partial T} &= a_1 + 2a_2 T, & \frac{\partial E}{\partial T} &= e_1 + 2e_2 T \\ \frac{\partial B}{\partial T} &= b_1 + 2b_2 T, & \frac{\partial D}{\partial T} &= -\left(\frac{d_1}{T^2} + \frac{2d_2}{T^3}\right) \end{aligned} \right\}. \quad (6.33)$$

In equation 6.33, values of the coefficients a_1 , a_2 , b_1 , b_2 , d_1 , d_2 , e_1 and e_2 along with other parameters are summarised in Tables (7.4 and 7.6); (7.8 and 7.9); (7.10 and 7.11) and (7.15) for the methane + hexadecane, methane + squalane, methane + cyclohexane and kryrox® oil respectively.

6.10.6 Uncertainty in mixture composition

For the binary systems, the relative uncertainty in preparing the mixtures contributed to the overall uncertainty of both density and viscosity through the partial derivatives. Since, for a homogeneous mixture composition x_1 is constant at all temperature and all pressures above the saturation line, therefore the only measured quantity that determine the mole fraction is a mass of sample as given by:

$$x_i = \frac{n_i}{\sum_{i=0}^N n_i} \quad (6.34)$$

where, n_i is the number of mole of component i defined as:

$$n_i = \frac{m_i}{M_i} \quad (6.35)$$

where, m_i and M_i are the mass and molar mass of component i respectively.

For a mixture of binary components, equation (6.34) can be re-written as follows:

$$x_1 = \frac{n_1}{n_1 + n_2} \quad (6.36)$$

Substituting equation (6.35) in (6.36) yields:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (6.37)$$

By taking the L.C.M, equation (6.37) further simplifies to:

$$x_1 = \frac{m_1 M_2}{m_1 M_2 + m_2 M_1} \quad (6.38)$$

Applying quotient rule to equation (6.38) to obtain the partial derivative of x_1 with respect to m_1 in equation (6.38) as follows:

$$\frac{\partial x_1}{\partial m_1} = \frac{(m_1 M_2 + m_2 M_1) \times \left[\frac{\partial(m_1 M_2)}{\partial m_1} \right] - (m_1 M_2) \times \left[\frac{\partial(m_1 M_2 + m_2 M_1)}{\partial m_1} \right]}{(m_1 M_2 + m_2 M_1)^2} \quad (6.39)$$

Evaluating the differentials in the square-brackets in equation (6.39) gives:

$$\frac{\partial x_1}{\partial m_1} = \frac{m_1 M_2^2 + M_2 M_1 m_2 - m_1 M_2^2}{(m_1 M_2 + m_2 M_1)^2} \quad (6.40)$$

Equation (6.40) reduces to:

$$\frac{\partial x_1}{\partial m_1} = \frac{M_2 M_1 m_2}{(m_1 M_2 + m_2 M_1)^2} \quad (6.41)$$

Similarly, the partial derivatives of x_1 with respect to m_2 can be obtained by differentiating equation (6.38) with respect to m_2 using quotient rule as follows:

$$\frac{\partial x_1}{\partial m_2} = \frac{(m_1 M_2 + m_2 M_1) \times \left[\frac{\partial(m_1 M_2)}{\partial m_2} \right] - (m_1 M_2) \times \left[\frac{\partial(m_1 M_2 + m_2 M_1)}{\partial m_2} \right]}{(m_1 M_2 + m_2 M_1)^2} \quad (6.42)$$

Evaluating the partial derivatives in the square-brackets in equation (6.42) yields:

$$\frac{\partial x_1}{\partial m_2} = \frac{-m_1 M_2 M_1}{(m_1 M_2 + m_2 M_1)^2} \quad (6.43)$$

Hence, in our case equations (6.41) and (6.42) provide the partial derivatives of the mole fraction of methane x_1 with respect to both mass of methane m_1 , and that of hexadecane

m_2 and by substituting the values of the two masses and molar masses, the partial derivatives can be evaluated.

The relative uncertainties of m_1 and m_2 influences the uncertainty of x_1 through the partial derivatives given by:

$$\left(\frac{\partial x_1}{\partial m_1}\right) = \left[\frac{m_2 M_1 M_2}{(m_1 M_2 + m_2 M_1)^2}\right] \text{ and } \left(\frac{\partial x_1}{\partial m_2}\right) = \left[\frac{-m_1 M_1 M_2}{(m_1 M_2 + m_2 M_1)^2}\right]. \quad (6.44)$$

These relations can be simplified as follows:

$$m_1 \left(\frac{\partial x_1}{\partial m_1}\right) = x_1(1 - x_1) \quad \text{and} \quad m_2 \left(\frac{\partial x_1}{\partial m_2}\right) = -x_1(1 - x_1); \quad (6.45)$$

or, in an alternative form, as follows:

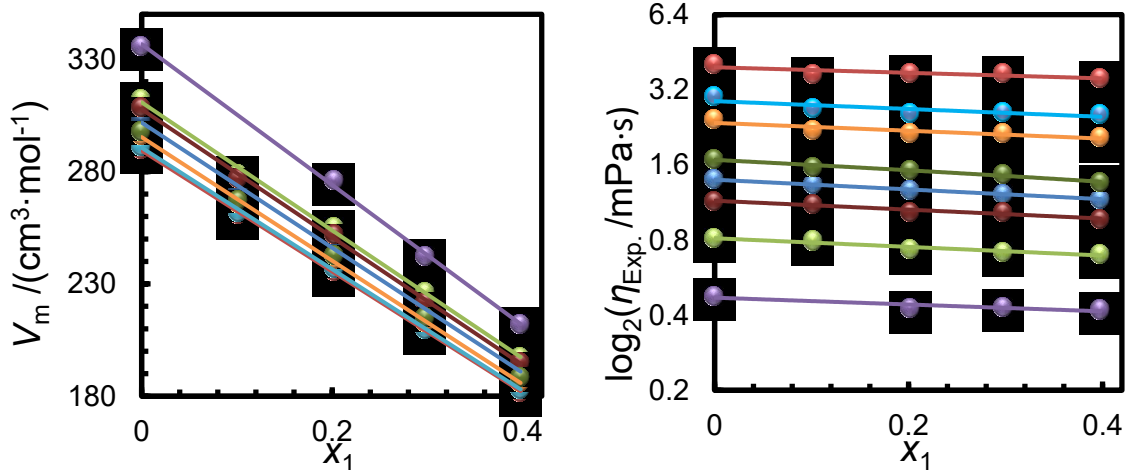
$$\left(\frac{\partial \ln x_1}{\partial \ln m_1}\right) = (1 - x_1) \quad \text{and} \quad \left(\frac{\partial \ln x_1}{\partial \ln m_2}\right) = -(1 - x_1) \quad (6.46)$$

Hence, the standard uncertainty $u(x_1)$ is given in terms of the relative standard uncertainties $u_r(m_1)$ and $u_r(m_2)$ of the two mass measurements as follows:

$$u(x_1) = x_1(1 - x_1) [u_r^2(m_1) + u_r^2(m_2)]^{1/2} \quad (6.47)$$

and the relative standard uncertainties of m_1 and m_2 were computed as $u_r(m_1) \approx 0.55\%$ and $u_r(m_2) \approx 0.05\%$ respectively. The standard uncertainty in mole fraction was obtained as $u(x_1) \approx 0.0013$ for the methane + hexadecane mixture at the highest mole fraction of methane ($x_1 = 0.4$).

To obtain the derivatives of the both density and viscosity with respect to the mole fraction, we first of all plot the graphs of experimental molar volume and viscosity at various temperature and pressure points as functions of mole fraction x_1 as shown in Figures 6.14(a) and (b).



(a)

(b)

Figure 6.14(a): Expression of molar volume (density) and (b) log to base two of viscosity as functions of mole fraction compositions for the methane + hexadecane system at T and p : ●, $T = 373$ K, $p = 40$ MPa; ●, $T = 473$ K, $p = 80$ MPa; ●, $T = 298$ K, $p = 20$ MPa; ●, $T = 473$ K, $p = 20$ MPa; ●, $T = 323$ K, $p = 40$ MPa; ●, $T = 323$ K, $p = 20$ MPa; ●, $T = 373$ K, $p = 20$ MPa; ●, $T = 373$ K, $p = 60$ MPa ———, trend lines and x_1 is mole fraction of methane

To each of the plot, in both Figures 6.14(a) and (b) we add regression lines that provide an adequate fit to the data. From Figure 6.14(a), we observed that linear function of x_1 fits the molar volume data reasonably well so that we can described the molar volume at constant temperature and pressure by the following empirical relation:

$$V_m = V_{m,0} + x_1 V_{m,1} \quad (6.48)$$

The mixture density is $\rho = (M/V_m)$, where $M = x_1 M_1 + (1 - x_1) M_2$ is the molar mass of the mixture and M_1 and M_2 are the molar masses of the two components. The derivative $(\partial \ln \rho / \partial x_1)$ is therefore given by:

$$\left(\frac{\partial \ln \rho}{\partial x_1} \right) = \left(\frac{\partial \ln M}{\partial x_1} \right) - \left(\frac{\partial \ln V_m}{\partial x_1} \right) = \left(\frac{M_1 - M_2}{M} \right) - \left(\frac{V_{m,1}}{V_m} \right). \quad (6.49)$$

Similarly, from figure 6.14(b), we observe that the logarithm of the viscosity may be represented as a linear function of mole fraction at constant temperature and pressure:

$$\ln \eta = \ln \eta_0 + x_1 B, \quad (6.50)$$

where η_0 is the viscosity at $x_1 = 0$. The derivative $(\partial \ln \eta / \partial x_1)$ is simply:

$$\left(\frac{\partial \ln \eta}{\partial x_1} \right) = B. \quad (6.51)$$

Equations (6.47) and (6.49) may be combined to determine the contribution to the uncertainty in ρ arising from the uncertainty in x_1 , while equations (6.47) and (6.51) may be combined to determine the contribution to the uncertainty in η arising from the uncertainty in x_1 .

Table 6.9 lists the values of $(\partial \ln \rho / \partial x_1)$ and $(\partial \ln \eta / \partial x_1)$ calculated from the coefficients in equations 6.49 and 6.51 at representative temperatures and pressure. Combining these values with the mole fraction uncertainty leads to estimates of the contribution of that uncertainty to the uncertainties in density and viscosity. Representative values are given in the table.

Table 6.9: Composition derivatives and contributions to the relative uncertainties of density and viscosity at representative temperatures and pressures

T/K	p/MPa	$(\partial \ln \rho / \partial x_1)$	$(\partial \ln \rho / \partial x_1)u(x_1)$ at $x_1 = 0.4$	$(\partial \ln \eta / \partial x_1)$	$(\partial \ln \eta / \partial x_1)u(x_1)$ at $x_1 = 0.4$
298	20	0.004	0.0015%	-0.257	0.03%
323	20	0.007	0.0009%	-0.363	0.05%
323	40	0.003	0.0004%	-0.362	0.05%
373	20	-0.010	0.0013%	-0.411	0.05%
373	40	-0.014	0.0019%	-0.45	0.06%
473	20	0.002	0.0002%	-0.316	0.04%
473	80	-0.031	0.0041%	-0.399	0.05%

From Table 6.9 it can be seen that the contributions of uncertainties in mole fractions to the overall uncertainties of both density and viscosity are small. For instance, it is evident from the table that even at the highest mole fraction of methane $x_1 = 0.4$ (i.e. the worst case scenario), the highest contributions to the uncertainty of both density and viscosity were found to be 0.004 % and 0.06% respectively. We can therefore conclude that the uncertainties in mole fractions are not a major source of error.

6.10.7 Overall uncertainty budget

For purposes of illustration, Tables 6.10 and 6.11 detail all known contributions to the standard relative uncertainties of the density and the viscosity at the median temperature and pressure of this study. For density, many terms contribute but the largest type-A terms is the uncertainty of the vacuum resonance frequency with an estimated standard uncertainty of 0.2 Hz. This estimate is based on a comparison of the calibration data with equation (6.6) over the full working temperature of the instrument. In the case of viscosity, there are several type-A uncertainties terms with roughly equal contribution. The uncertainty budgets also includes estimates of type-B relative uncertainties, of 0.06 % for density and 0.6 % for viscosity, which were estimated from the results obtained with the standard calibration fluid.

Table 6.10: Uncertainty budget for the density of pure hexadecane and its binary mixture at the median state point in terms of standard uncertainty $u(z)$ of dimensionless parameter z and arising contribution $u_r(\rho)$ to the overall standard relative uncertainty of density

Dimensionless quantity	z	$u(z)$	$10^2 u_r(z)$	$10^2 u_r(\rho)$
T/K	398.15	0.1	0.025	0.007
p/MPa	40.0	0.2	0.5	0.019
f_{res}/Hz	716.27	0.04	0.005	0.031
Ω_{res}	17.71	0.04	0.24	0.011
$f_{0,\text{vac}}/\text{Hz}$	850.6	0.2	0.023	0.142
m/kg	0.403 625	1.5×10^{-6}	0.0004	0.0003
V_0/cm^3	142.055	0.003	0.0021	0.002
$R_0/\mu\text{m}$	75.5	0.1	0.13	0.007
L_0/mm	66.13	0.01	0.015	0.002
E_0/GPa	390	10	2.6	0.001
$\rho_s/(\text{kg}\cdot\text{m}^{-3})$	19250	50	0.26	0.031
α_w/K^{-1}	4.5×10^{-6}	0.32×10^{-6}	7	0.001
β_w/MPa^{-1}	3.24×10^{-6}	0.03×10^{-6}	1	0.000
$\varepsilon_w/\text{K}^{-1}$	-9.7×10^{-5}	0.5×10^{-5}	5	0.001
α_s/K^{-1}	23.6×10^{-6}	0.7×10^{-6}	3	0.019
β_s/MPa^{-1}	14.3×10^{-6}	0.7×10^{-6}	5	0.002
x	0.3979	1.33×10^{-3}	0.33	0.002
$\rho/(\text{kg}\cdot\text{m}^{-3})$	734.5	0.44 ^a	0.06	0.060
Overall combined standard relative uncertainty at median T and p				0.16
Overall expanded uncertainty at coverage factor $k = 2$ at median T and p				0.32

Table 6.11: Uncertainty budget for the viscosity of pure hexadecane and mixtures at the median state point in terms of standard uncertainty $u(z)$ of dimensionless parameter z and arising contribution $u_r(\eta)$ to the overall standard relative uncertainty of viscosity

Dimensionless quantity z	z	$u(z)$	$10^2 u_r(z)$	$10^2 u_r(\eta)$
T/K	398.15	0.1	0.025	0.10
p/MPa	40.0	0.2	0.5	0.19
f_{res}/Hz	716.27	0.04	0.005	0.01
Ω_{res}	17.71	0.04	0.24	0.24
$\rho/(\text{kg}\cdot\text{m}^{-3})$	734.5	1.2	0.16	0.33
$R/\mu\text{m}$	75.5	0.1	0.13	0.27
$\rho_w/(\text{kg}\cdot\text{m}^{-3})$	19250	50	0.26	0.09
Δ_0	65×10^{-6}	20×10^{-6}	31	0.19
α_w/K^{-1}	4.5×10^{-6}	0.32×10^{-6}	7	0.01
β_w/Mpa^{-1}	3.24×10^{-6}	0.03×10^{-6}	1	0.00
x	0.3979	1.33×10^{-3}	0.33	0.06
$\eta/(\text{mPa}\cdot\text{s})$	1.046	0.006 ^a	0.6	0.60
Overall combined standard relative uncertainty at median T and p				0.84
Overall expanded uncertainty at coverage factor $k = 2$ at median T and p				1.68

It is important to note that, the robust analytical uncertainty analysis presented in this chapter is unprecedented, and it is a significant contribution to the field of vibrating-wire viscometry.

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Results and Discussion

7.1 Introduction

The vibrating-wire viscometer-densimeter described in section 5.1 was used for simultaneous viscosity and density measurements on pure components and binary asymmetric hydrocarbon mixtures. The binary mixtures investigated in this work are the mixtures of higher molecular-weight components with dissolved gas (methane in this case). The heavy hydrocarbon components were chosen from representatives of each of the saturated aliphatic group of hydrocarbons namely: the straight chain, the branched chain and also the cyclo-group. *n*-Hexadecane was chosen from the straight chain group, whereas 2,6,10,15,19,23-hexamethyltetracosane (squalane) and cyclohexane were selected from the straight chain and the cyclo groups respectively as there were very few (in some cases no) reported literature data on the viscosity of mixtures of these compounds with dissolved methane to the author's knowledge. In all the three binary mixtures, a total of four mole fractions of methane were studied in the temperature range (298 to 473) K at pressures up to 200 MPa. The estimated expanded relative uncertainties for these measurements were within 2.1 % for viscosity and 0.34 % for density with a coverage factor *k* of 2. The subsequent sections present the results for each of the systems investigated.

Prior to the commencement of measurement on any mixture, literature data on vapour-liquid equilibrium (VLE) of the mixture covering the temperature, pressure and composition range of interest were collected. Where there were no VLE data available, or the data does not cover the desired temperature, pressure and/or composition range, the Peng-Robinson^[1] Equation of State (PR^[1]-EoS) in Aspen was employed after tuning the binary interaction parameters to extend or predict the data to the required region. The VLE data is necessary in order to ensure all measurements are conducted within the single-phase liquid region.

It is important to note here that measurements are systematically carried-out along isotherms starting from the lower temperature to the higher ones. Furthermore, the pressure is progressively increases starting from just above the minimum saturation pressure of the mixture to the highest achievable pressure along a given isotherm and then, a check measurement is conducted along each isotherm by re-measuring at lower pressure. The essence of the check measurement was to determine if there is any change in the properties of fluid and/or the device settings has been compromised during the experiment. In any case, the repeatability of the check measurements has to be within the $10^{-2}\eta$ and $10^{-3}\rho$ tolerances from the initial measurements before the value is recorded.

7.2 Chemicals

The materials used in this work are detailed in Table 7.1. Although no additional purification on the samples were carried out, however the purity of the pure *n*-hexadecane, squalane and cyclohexane were analyzed by running a gas chromatography-mass spectrometry (GC-MS) on the samples.

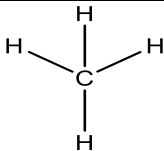
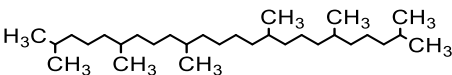
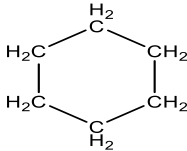
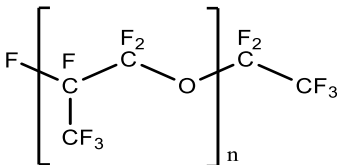
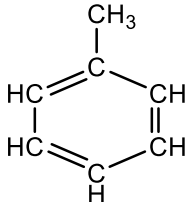
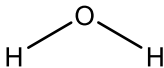
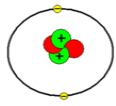
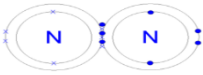
Table 7.1: Description of Chemical Samples^a

Chemical Name	Source	Purity as Supplied ^a	Estimated Purity	Analysis Method	Additional Purification
<i>n</i> -hexadecane	S. Aldrich	$w > 99.00 \%$	99.83 %	GC-MS ^b	degassing
cyclohexane	S. Aldrich	$w \geq 99.50 \%$	99.72 %	GC-MS ^b	degassing
squalane	S. Aldrich	$w = 99.00 \%$	98.70 %	GC-MS ^b	degassing
Toluene	S. Aldrich	$w = 99.00 \%$	-	-	degassing
methane	BOC	$x \geq 0.99995$	-	-	none
helium	BOC	$x \geq 0.999$	-	-	none
krytox [®] GPL 102	DuPont	$w = 99.90 \%$	-	-	degassing
S20 Standard	Paragon	-	-	-	-

^aNotation: w is mass fraction and x is mole fraction. ^aPurities are as stated by the supplier except where an analysis method is specified.

^bGas chromatography-mass spectrometry

Table 7.2: Properties of Chemical Samples used

name	Chemical Formula	M_{wt} (g/mol)	Chemical structure
Methane	CH_4	16.04	
<i>n</i> -Hexadecane (<i>n</i> -cetane)	$C_{16}H_{34}$	226.44	
2,6,10,15,19,23-Hexamethyltetracosane (squalane)	$C_{30}H_{50}$	422.83	
Cyclohexane	C_6H_{12}	84.16	
Perfluoropolyether Krytox®	$F[CF(CF_3)CF_2O]_n CF_2CF_3$	1720	
Toluene	C_7H_8	92.14	
De-ionised water	H_2O	18.02	
Helium	He	4.00	
Nitrogen	N_2	14	
S20 viscosity standard			

7.3 Data Correlation

The experimental density data obtained for each composition were correlated using the widely known modified Tait equation^[2]. This correlation was applied to the individual

compositions by expressing density ρ as a function of temperature and pressure and a global surface fit was obtained.

$$\rho / (\text{kg} \cdot \text{m}^{-3}) = \rho_0 \left[1 - C \log_{10} \left(\frac{p + B}{p_0 + B} \right) \right]^{-1}, \quad (7.1)$$

where $p_0 = 0.1$ MPa, ρ_0 is the density at $p = p_0$, and C is a constant. The parameters ρ_0 and B are expressed as quadratic functions in temperature as follows:

$$\rho_0 / (\text{kg} \cdot \text{m}^{-3}) = \sum_{i=0}^2 a_i (T / T_0)^i, \quad (7.2)$$

and

$$B / \text{MPa} = \sum_{i=0}^2 b_i (T / T_0)^i, \quad (7.3)$$

where $T_0 = 293$ K and the parameters C , a_i 's and b_i 's in equations 7.1, 7.2 and 7.3 are obtained by a non-linear optimisation technique that minimised the absolute average relative deviation ($\Delta_{\text{AAD},X}$) from the experimental data for a property X defined by:

$$\Delta_{\text{AAD},X} = \frac{1}{N} \sum_{i=1}^N \left(\frac{|X_{i,\text{Exp.}} - X_{i,\text{Fit}}|}{X_{i,\text{Exp.}}} \right), \quad (7.4)$$

where, N is the total number of points, $X_{i,\text{Exp.}}$ is the experimental datum, $X_{i,\text{Fit}}$ is calculated from the correlation at exactly the same state point. The maximum absolute relative deviations ($\Delta_{\text{MAD},X}$) and relative bias ($\Delta_{\text{Bias},X}$) defined in equations 4.48 and 4.49 were also calculated for each mole fraction.

Similarly, the experimental viscosity results were correlated using the Tait-Andrade correlation given by:

$$\eta / (\text{mPa} \cdot \text{s}) = A_\eta \exp \left(\frac{B_\eta}{T + C_\eta} \right) \left(\frac{p + E}{p_0 + E} \right)^D, \quad (7.5)$$

where $p_0 = 0.1$ MPa, D and E are functions of temperature expressed in the following forms:

$$D = \sum_{i=0}^2 d_i (T / T_0)^{-i}, \quad (7.6)$$

and,

$$E / \text{MPa} = \sum_{i=0}^2 e_i (T / T_0)^i. \quad (7.7)$$

Again, $T_0 = 298.15$ K and the optimisation was carried out individually on each mixture composition and the coefficients of equations 7.5 to 7.7 are tabulated both for pure components and each individual mixture composition in the subsequent sections.

7.4 Pure *n*-hexadecane

Although the density and viscosity of pure *n*-hexadecane liquid were previously measured by Ciotta^[3] in our group using the same device operated in a relative mode. Nevertheless, new density and viscosity measurements on the pure *n*-hexadecane were conducted in the temperature range (298.15 to 473.15) and pressure up to 80 MPa with the VWVD operated in an essentially absolute mode. The essence of repeating these measurements was to allow us to be able to compare the results from these two independent measurements using the same apparatus and also to serve as further validation of the device. For the first isotherm ($T = 298.15$ K), measurements were only possible up to a maximum pressure limit $p = 30$ MPa beyond which the hexadecane froze in the inlet lines. Similarly, for other isotherms, the maximum pressures were limited to $p_{\max} < 100$ MPa, the approximate freezing pressure of *n*-hexadecane at the maximum operating temperature of the pressure transducer in the fluid handling unit and the inlet lines. A quick observation of the results showed the usual trend of both density and viscosity decrease with temperature and increase with pressure. Figures 7.1 and 7.2 illustrate these trends for density and viscosity of *n*-hexadecane as functions of pressure and temperature.

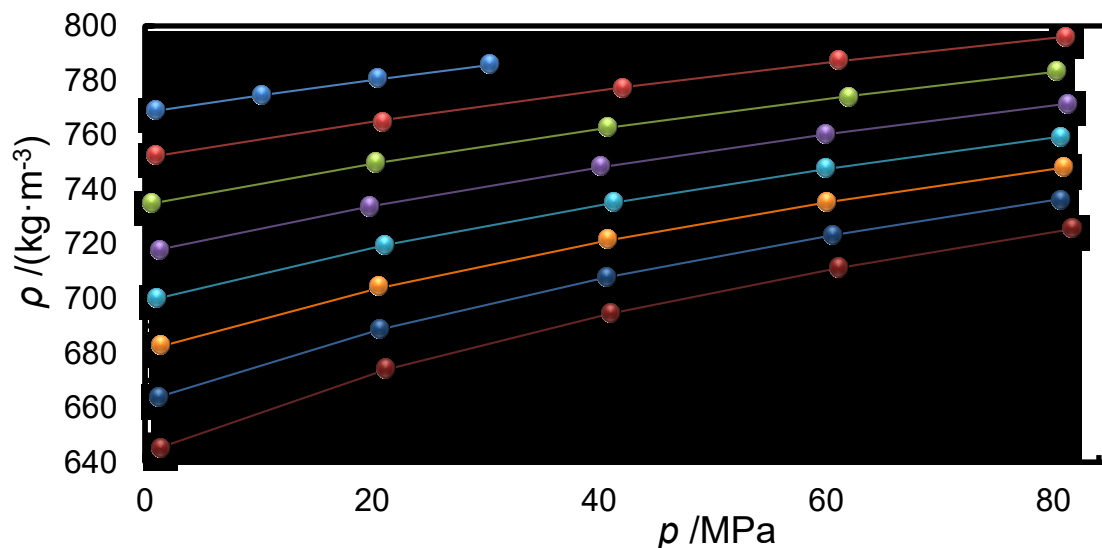


Figure 7.1: Experimental density $\rho_{\text{Exp.}}$ of pure hexadecane as function of pressure p /MPa. $\bullet$, $T = 298$ K; $\bullet$, $T = 323$ K; $\bullet$, $T = 348$ K; $\bullet$, $T = 373$ K; $\bullet$, $T = 398$ K; $\bullet$, $T = 423$ K; $\bullet$, $T = 448$ K and $\bullet$, $T = 473$ K. lines —, represent Tait correlation, equation 7.1

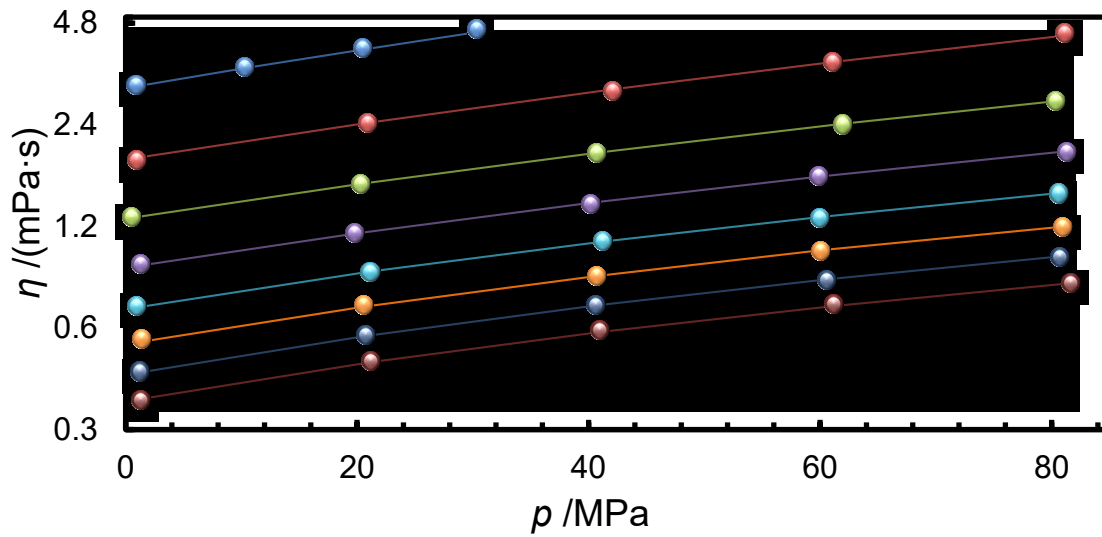


Figure 7.2: Experimental viscosity $\eta_{\text{Exp.}}$ of pure hexadecane as function of pressure p /MPa. ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 348$ K; ●, $T = 373$ K; ●, $T = 398$ K; ●, $T = 423$ K; ●, $T = 448$ K and ●, $T = 473$ K. lines —, represent Tait-Andrade correlation, equation 7.5

The new results were compared with the old data and using the correlating equations (7.1 and 7.5) and very good agreements were observed between the two datasets as shown in Figures 7.3 and 7.4 for density and viscosity respectively. The coefficients of the correlations as well as the statistical measures described in equations (4.47 to 4.49) were tabulated as shown in Tables (7.4 and 7.6) for density and viscosity respectively. The good agreement observed between the two datasets further validates the VWVD device and gave us the confidence to proceed the measurement campaign on the mixtures.

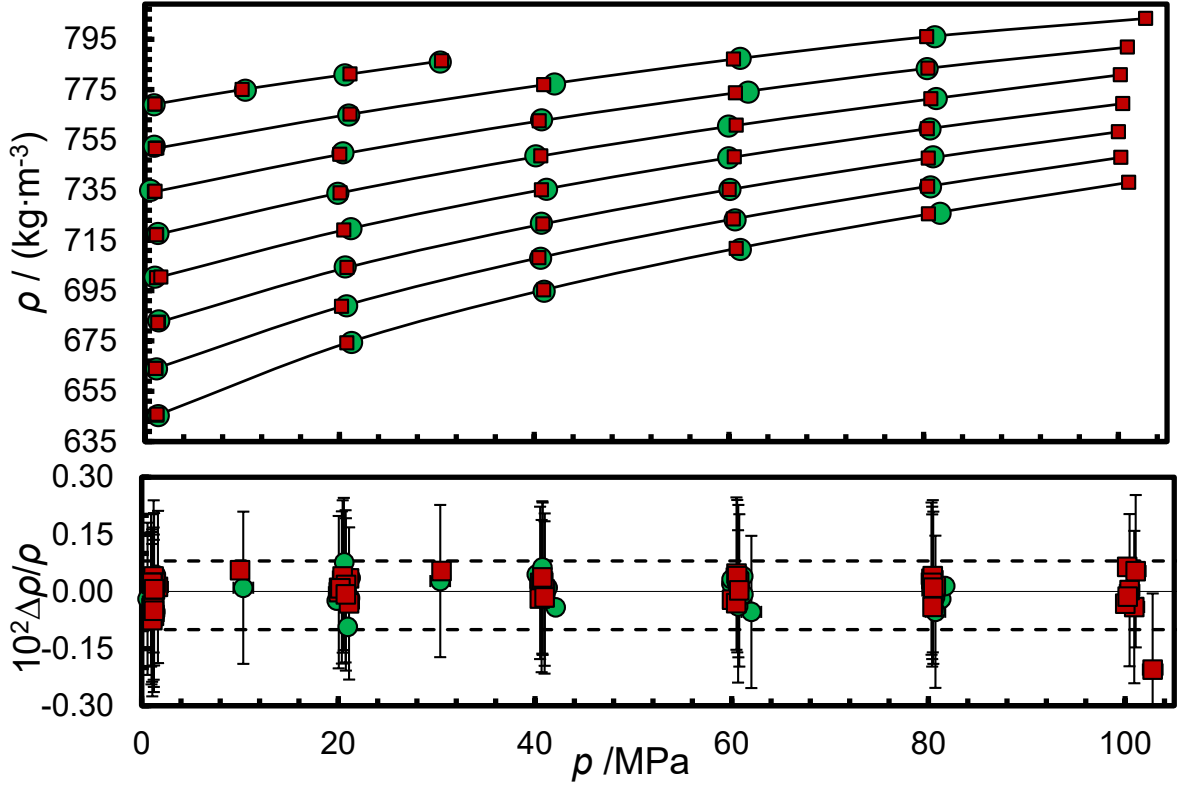


Figure 7.3: Comparison of the new density data (this work) obtained by absolute measurement against Ciotta's[3] data obtained by relative measurement. ●, this work; ■ Ciotta^[4]. 2010 and the lines —, Tait correlation equation 7.1

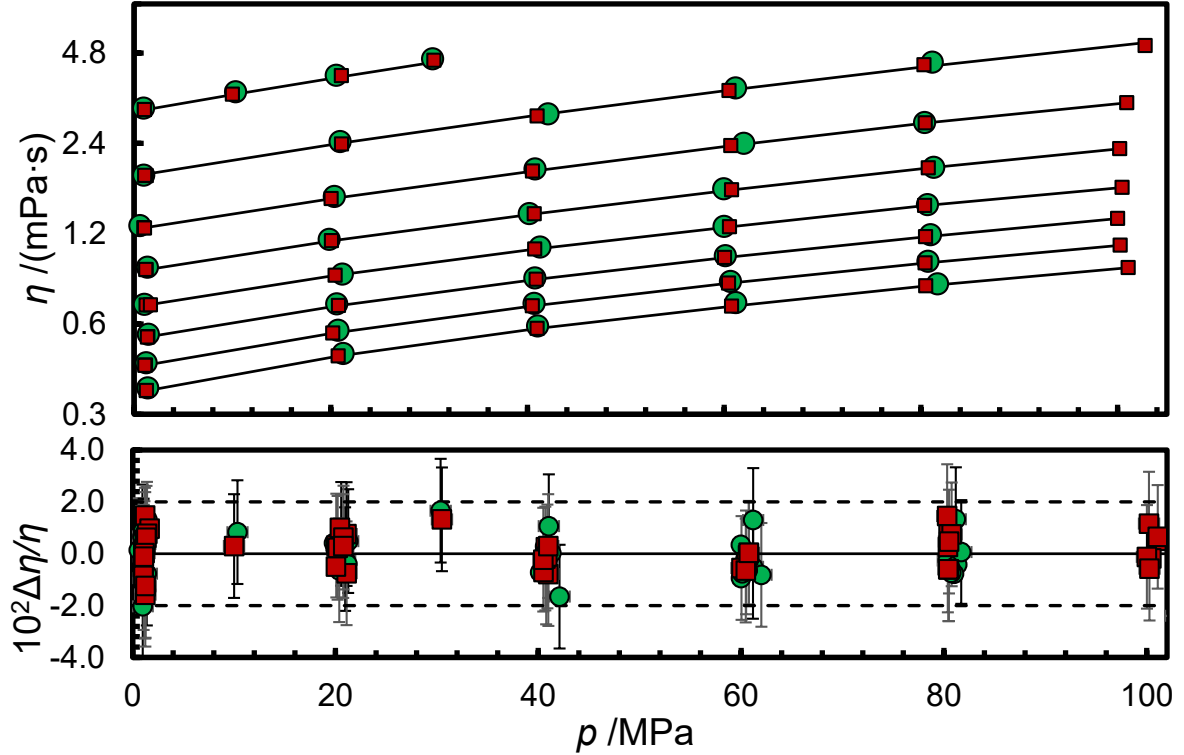


Figure 7.4: Comparison of the new viscosity data (this work) obtained by absolute measurement against Ciotta's[3] data obtained by relative measurement. ●, this work; ■ Ciotta^[4]. 2010 and the lines —, Tait-Andrade correlation equation 7.5

7.4.1 Comparison with Literature Data

There are a number of datasets on density and viscosity of the pure *n*-hexadecane available in the literature reported by different authors using different techniques. The new results were compared with some selected datasets from the literature covering the temperature and pressure range of interest. For density, the new datasets obtained in this work described by equation 7.1 were compared with the following literature data^[3, 5-16] as shown in Figure 7.5 and Table 7.3.

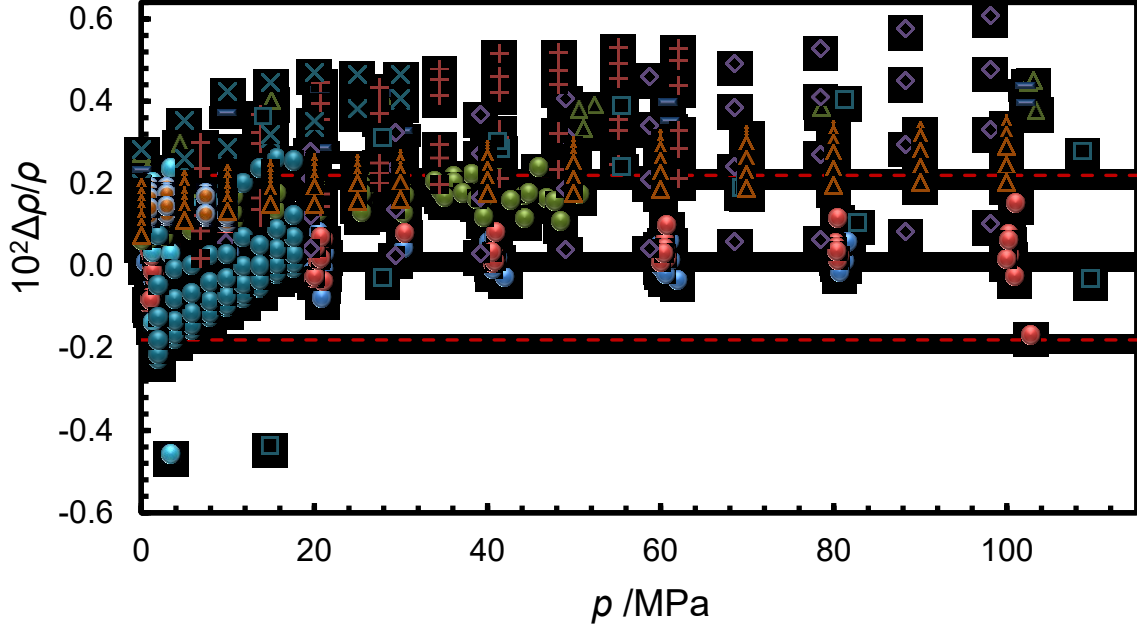


Figure 7.5: Fractional deviation of density of pure *n*-hexadecane from equation 7.1 as a function of pressure p : ● This work; ● Ciotta^[3]; ● Dymond *et al.* ^[6]; ● Matthews *et al.*^[7]; ▲, Outcalt *et al.*^[17]; —, Tanaka *et al.*^[9]; ◆, Kuss *et al.*^[13]; ●, Glaser *et al.*^[14]; +, Amorim *et al.*^[12]; ○, Banipal *et al.*^[16]; ■, Baled *et al.*^[15]; ×, Chang *et al.*^[10]; △, Khasanshin *et al.*^[11]; and — — — relative uncertainty of equation 7.1

Similarly, the density results from the present work along with some literature datasets were compared with the recent equation of state by Romeo and Lemmon^[18]. These comparisons were illustrated in Figure 7.6 and Table 7.3. However, the equation was applied to the experimental data within its validity range of temperature ($291.33 \leq T / \text{K} \leq 800$), $p \leq 50$ MPa and density $\rho \leq 775.11 \text{ kg} \cdot \text{m}^{-3}$.

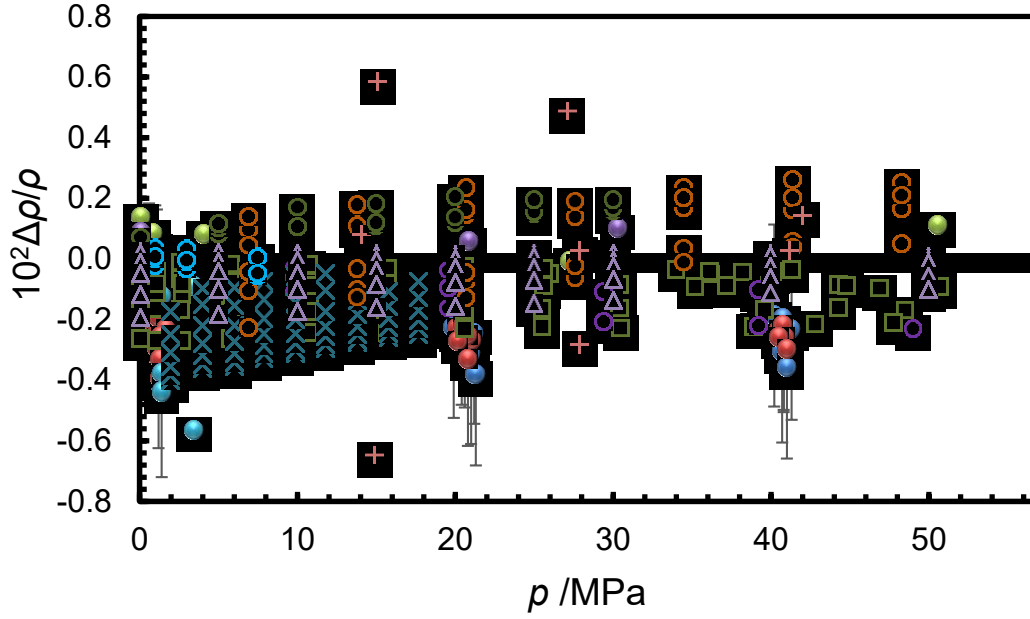


Figure 7.6: Fractional deviation of density of pure *n*-hexadecane from equation of state of Romeo and Lemmon^[18] as a function of pressure p : ● This work; ● Ciotta^[3]; ● Dymond *et al.*^[6]; ● Matthews *et al.*^[7]; □, Outcalt *et al.*^[17]; ●, Tanaka *et al.*^[9]; ●, Kuss *et al.*^[13]; ×, Glaser *et al.*^[14]; ○, Amorim *et al.*^[12]; ○, Banipal *et al.*^[16]; +, Baled *et al.*^[15]; ○, Chang *et al.*^[10]; and △, Khasanshin *et al.*^[11]

As can be seen from Figure 7.6 and Table 7.3 the equation of state (EoS)[18] of Romeo and Lemmon^[18] described our density results for pure hexadecane with average absolute deviations $\Delta_{\text{AAD},p}$ of about 0.2 %. Condining the mutual uncertainties of our measurements and that of the equation, it can be said our data datasets are in agreement with this EoS^[18] as well as the other literature datasets shown in Figure 7.6 and Table 7.3.

Table 7.1: Deviations of the Literature Density Data for *n*-Hexadecane

Source	Deviations from Equation 7.1			Deviations from Romeo and Lemmon ^[18]		
	$10^2 \Delta_{\text{AAD},p}$	$10^2 \Delta_{\text{bias},p}$	$10^2 \Delta_{\text{MAD},p}$	$10^2 \Delta_{\text{AAD},p}$	$10^2 \Delta_{\text{bias},p}$	$10^2 \Delta_{\text{MAD},p}$
This Work	0.03	0.00	0.09	0.24	-0.24	0.42
Ciotta ^[3]	0.03	0.00	0.21	0.23	-0.23	0.27
Dymond <i>et al.</i> ^[5]	0.12	0.17	0.92	0.09	0.08	0.14
Tanaka <i>et al.</i> ^[9]	0.07	0.32	0.42	0.06	0.06	0.10
Dymond <i>et al.</i> ^[6]	0.08	0.29	0.43	0.07	0.06	0.14
Matthews <i>et al.</i> ^[7]	0.14	0.01	0.48	0.32	-0.32	0.56
Outcalt <i>et al.</i> ^[8]	0.03	0.12	0.22	0.10	-0.10	0.27
Kuss <i>et al.</i> ^[13]	0.20	0.32	0.95	0.10	-0.10	0.23
Glaser <i>et al.</i> ^[14]	0.10	0.00	0.25	0.23	-0.23	0.40
Amorim <i>et al.</i> ^[12]	0.11	0.30	0.51	0.13	0.07	0.26
Banipal <i>et al.</i> ^[16]	0.02	0.13	0.18	0.02	0.00	0.08
Baled <i>et al.</i> ^[15]	0.15	0.22	0.50	0.28	0.05	0.65
Chang <i>et al.</i> ^[10]	0.07	0.33	0.45	0.13	0.13	0.20
Khasanshin <i>et al.</i> ^[11]	0.05	0.22	0.36	0.05	-0.04	0.19

Table 7.4: Statistical Parameters for the Density Correlation of $x\text{CH}_4$ (1) + $(1-x)\text{C}_{16}\text{H}_{34}$ (2) Mixtures at Different Compositions and Coefficients of Equations (7.1, 7.2 and 7.3)

Coefficient	$x_1 = 0.0$	$x_1 = 0.1013$	$x_1 = 0.2021$	$x_1 = 0.2976$	$x_1 = 0.3979$
C	1.986×10^{-1}	2.036×10^{-1}	2.036×10^{-1}	2.036×10^{-1}	2.036×10^{-1}
a_0	9.530×10^2	9.699×10^2	9.982×10^2	8.920×10^2	1.011×10^3
a_1	-1.665×10^2	-1.907×10^2	-2.310×10^2	-6.040×10^1	-2.445×10^2
a_2	-1.784×10^1	-4.460×10^0	1.646×10^0	-6.221×10^1	6.576×10^0
b_0	3.896×10^2	2.975×10^2	3.813×10^2	2.513×10^2	4.035×10^2
b_1	-3.879×10^2	-2.421×10^2	-3.788×10^2	-1.800×10^2	-4.066×10^2
b_2	1.016×10^2	4.764×10^1	9.873×10^1	2.488×10^1	1.074×10^2
$10^2 \Delta_{\text{AAD},p}$	0.03	0.05	0.03	0.11	0.03
$10^2 \Delta_{\text{MAD},p}$	0.20	0.16	0.07	0.30	0.07
$10^2 \Delta_{\text{bias},p}$	0.00	0.00	0.00	0.00	0.00

Similarly, the new viscosity datasets for the pure *n*-hexadecane were compared with some available literature data in the temperature and pressure range of interest. Data in literature are at pressures between (0.1 and 425) MPa and at temperatures between (303 and 564) K. In Figure 7.7 and Table 7.5, we compare the available literature data for the

viscosity of *n*-hexadecane with eq (7.1) in its range of validity. The viscosity data generally agree with the result of this work, and only in two cases are the mean absolute relative deviation larger than 2 %. The data presented in by Ducoulombier *et al*[19] and Baled *et al* were respectively gathered with a falling-body and a rolling-ball viscometer which necessitates density inputs in order to determine the dynamic viscosities and there was no indication of the uncertainty of the density values used.

Figure 7.7 and Table 7.5 compare some selected literature datasets for the viscosity of *n*-hexadecane with equation 7.5 in its range of validity.

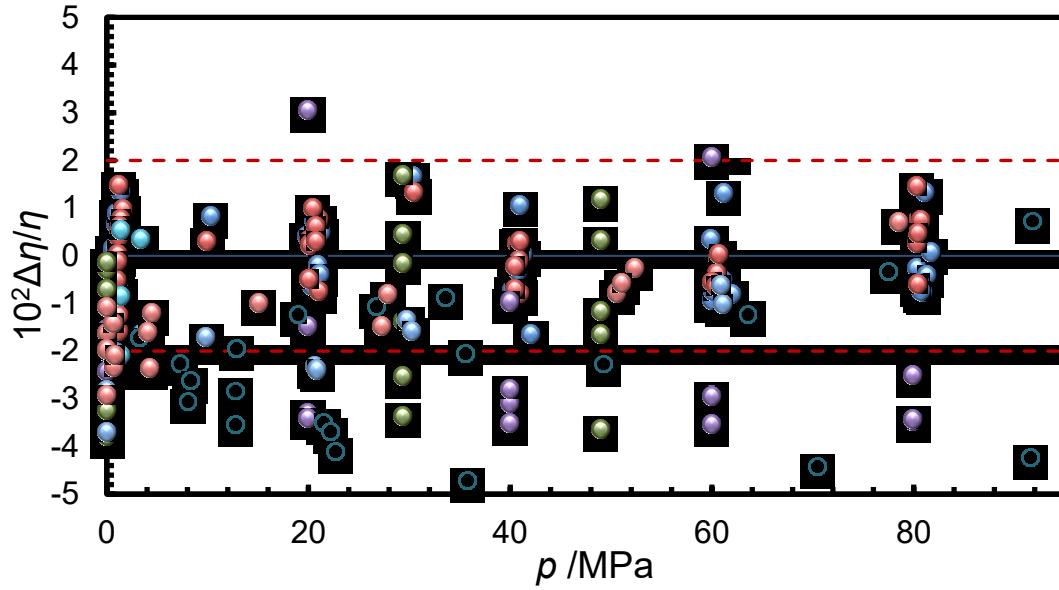


Figure 7.7: Fractional deviation of viscosity of pure *n*-hexadecane from equation 7.5 as a function of pressure p : ● This work; ● Ciotta^[3]; ● Dymond *et al.* ^[6]; ● Matthews *et al.* ^[7]; ● Rastorguev *et al.* ^[20]; ●, Ducoulombier *et al.* ^[19]; ○, Baled *et al.* ^[21] ^[21] ^[26] ^[26] ^[26]; Tanaka *et al.* ^[9]; and - - - relative uncertainty of equation 7.5

From Figure 7.7 it can be seen that most of the viscosity data agree with the result of this work, and only in two cases are the mean absolute relative deviation larger than 2 %. The data presented in by Ducoulombier *et al*[19] and Baled *et al* were respectively gathered with a falling-body and a rolling-ball viscometer which necessitates density inputs in order to determine the dynamic viscosities and there was no indication of the uncertainty of the density values used.

Table 7.5: Deviation of the Literature Viscosity Data for n-Hexadecane from Equation 7.5

Source	$10^2 \Delta_{AAD, \eta}$	$10^2 \Delta_{bias, \eta}$	$10^2 \Delta_{MAD, \eta}$
This Work	0.7	0.0	2.0
Ciotta ^[3]	0.6	-1.4	3.9
Rastorguev <i>et al.</i> ^[22]	1.5	-1.2	3.8
Tanaka <i>et al.</i> ^[9]	1.2	-1.4	3.7
Dymond <i>et al.</i> ^[6]	1.2	-0.8	3.5
Ducoulombier <i>et al.</i> ^[19]	2.1	-1.5	7.6
Matthews <i>et al.</i> ^[7]	1.0	-0.7	2.1
Baled <i>et al.</i> ^[21]	2.1	-1.9	4.7

Table 7.6: Statistical Parameters for the Viscosity Correlation of $x\text{CH}_4$ (1) + (1-x) $\text{C}_{16}\text{H}_{34}$ (2) Mixtures at Different Compositions and Coefficients of Equations (7.5, 7.6 and 7.7)

Coefficient	$x_1 = 0$	$x_1 = 0.1013$	$x_1 = 0.2021$	$x_1 = 0.2976$	$x_1 = 0.3979$
A_η	2.693×10^{-2}	2.887×10^{-2}	3.562×10^{-2}	3.119×10^{-2}	5.233×10^{-2}
B_η	1.006×10^3	9.544×10^2	7.926×10^2	9.043×10^2	6.305×10^2
C_η	-8.621×10^1	-9.214×10^1	-1.182×10^2	-9.837×10^1	-1.404×10^2
d_0	3.112×10^0	-7.183×10^0	3.761×10^0	2.964×10^2	1.678×10^5
d_1	-7.475×10^0	1.438×10^1	-5.856×10^0	-1.518×10^2	-2.414×10^5
d_2	6.739×10^0	-2.743×10^0	2.978×10^0	-1.492×10^2	6.555×10^4
e_0	7.346×10^2	1.633×10^3	2.132×10^2	-6.587×10^4	-1.115×10^7
e_1	-8.044×10^2	-1.602×10^3	-2.698×10^2	8.963×10^4	1.120×10^7
e_2	2.441×10^2	3.788×10^2	1.215×10^2	-2.414×10^4	-7.812×10^5
$10^2 \Delta_{AAD, \eta}$	0.81	1.14	0.76	0.60	0.82
$10^2 \Delta_{MAD, \eta}$	2.50	3.36	1.73	1.78	1.98
$10^2 \Delta_{bias, \eta}$	0.01	0.05	0.01	0.01	0.01

7.5 Methane (1) + hexadecane (2)

The first binary system studied was the CH_4 (1) + $\text{C}_{16}\text{H}_{34}$ (2) at four different mole fractions of methane $x = (0.1013, 0.2021, 0.2976 \text{ and } 0.3979)$ in the temperature range of (298 to 473) K and at pressures up to 200 MPa. VLE data for $[x\text{CH}_4$ (1) + (1-x) $\text{C}_{16}\text{H}_{34}$ (2)], in the temperature range of (373.15 to 623.15) K was obtained from Sultanov *et al.*^[23] and using the PR[1]-EoS the dataset was extended to the desired lowest working temperature of 313.15 K as shown in Figure 7.8.

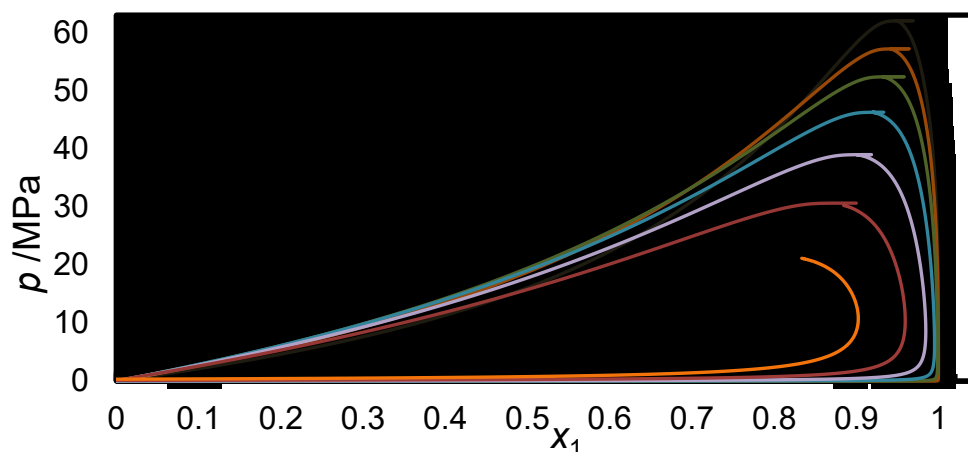


Figure 7.8: Phase diagram of $x\text{CH}_4+(1-x)\text{C}_{16}\text{H}_{34}$ mixtures. Symbols represent literature data from Sultanov *et al.*^[23] ●, $T = 373\text{ K}$; ●, $T = 423\text{ K}$; ●, $T = 473\text{ K}$; ●, $T = 523\text{ K}$; ●, $T = 573\text{ K}$; ●, $T = 623\text{ K}$ and lines —, represent Peng-Robinson^[1] equation of state in Aspen Hysys

The methane gas used in this work was a research grade obtained from the BOC gas while the liquid n-hexadecane was sourced from Sigma Aldrich with the claimed percentage mass purity of greater than 99 %. Although, no additional purification was carried out on the pure n-hexadecane. However, a gas-chromatography mass-spectrometry (GC-MS) analysis was conducted using a column with the specifications shown in Table 7.7. The aim of the (GC-MS) analysis was two folds: 1). to estimate the actual percentage purity of the sample and 2). to identify the probable impurities present in the sample so as to determine their effects on the final results. It was estimated from the chromatogram that the sample purity was 99.83 % n- $\text{C}_{16}\text{H}_{34}$ and based on the mass spectrum of the impurities it is highly likely that the remaining 0.17 % was predominantly n- $\text{C}_{19}\text{H}_{40}$ and its effects on both density and viscosity results are insignificant. Figures 7.9 and 7.10 show the chromatogram and the mass spectrum of the dominant impurities respectively.

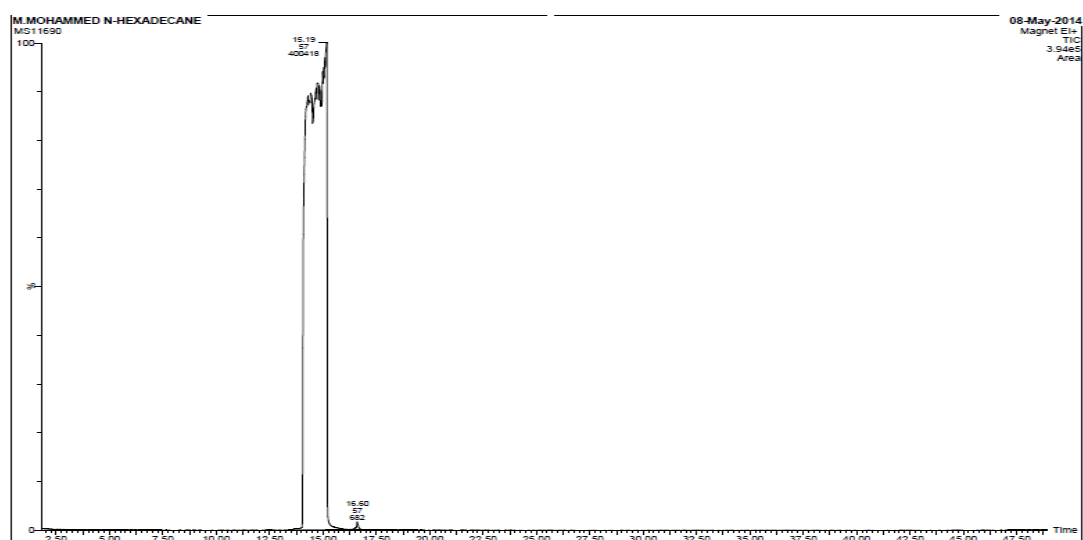
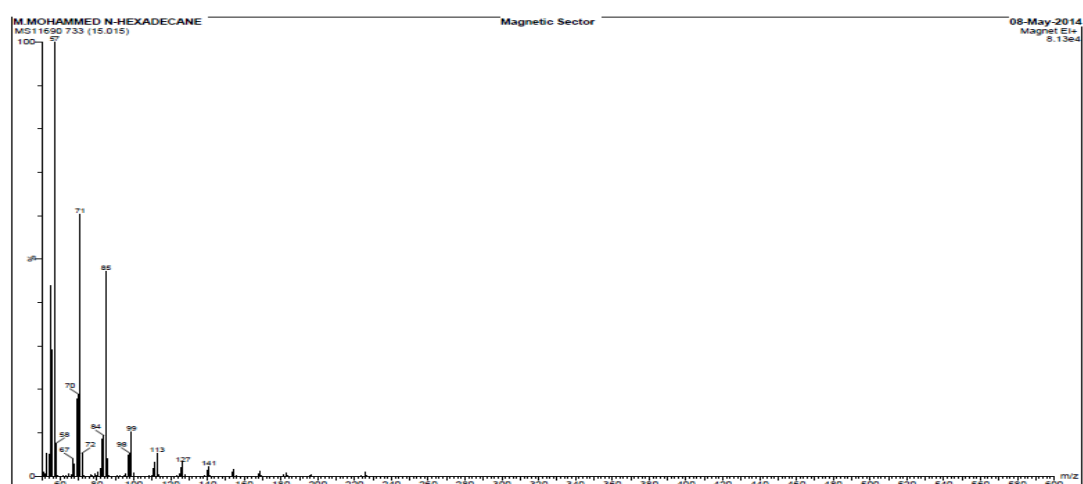

 Figure 7.9: The chromatogram of the pure *n*-hexadecane


Figure 7.10: The mass spectrum of the dominant impurities present in the pure hexadecane

Table 7.7: Properties of the gas chromatography GC Column

Analysis:	GC-MS
Technique:	Magnet EI + TIC
	BPX5: $L = 30$ m: $d = 0.25$
Column type:	mm
Carrier gas:	Helium; $G = 1$ ml·min ⁻¹
T ramp:	5 K·min ⁻¹ (from 333.15 to 593.15 K)
Hold time t :	1 min

Four different compositions of the binary mixture of CH₄ (1) + C₁₆H₃₄ (2) were studied with x_1 (= 0.1013, 0.2021, 0.2976 and 0.3979). The viscosity and density of each composition were measured simultaneously along isotherms at nominal temperatures of (298.15, 323.22, 373.26, 423.31 and 473.17) K with pressures up to 80 MPa. Table 7.14 presents

the properties of the vibrating-wire used in these measurements. Figure 7.11 shows a plot of experimental viscosity of this binary system at 373 K against molar volume, whereas Tables B.1 to B.5 in appendix B present the full results. The experimental temperatures shown in the tables slightly differed from the nominal values due to slight fluctuations of the heating system but were constant to within ± 0.02 K. It was observed that the addition of methane significantly lower the viscosity and of the pure *n*-hexadecane as expected.

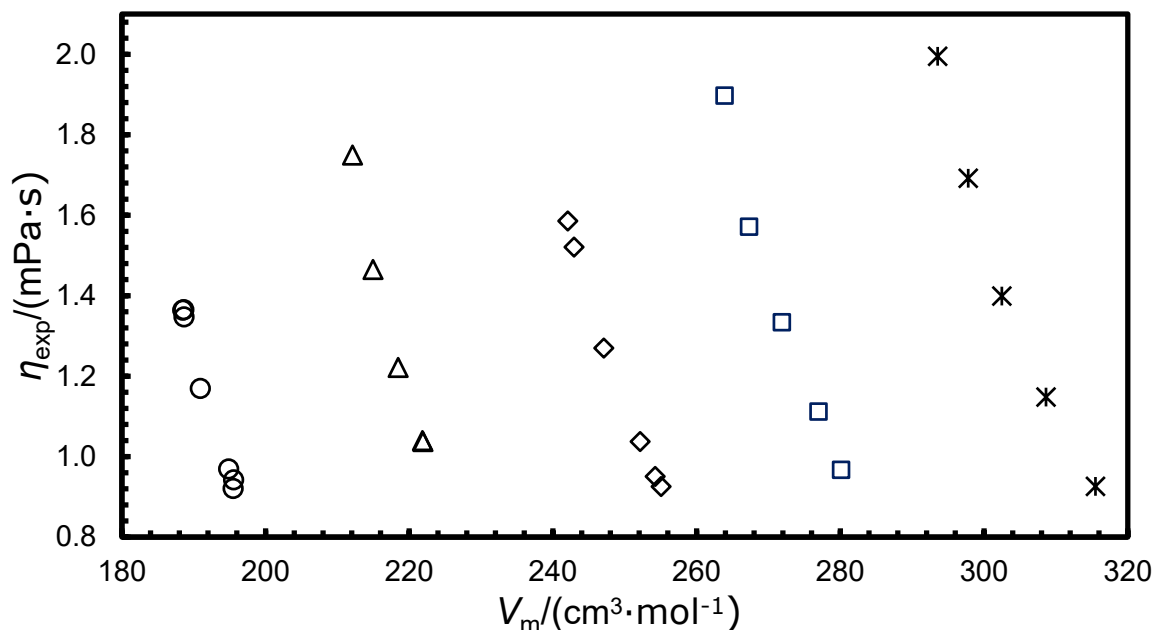


Figure 7.11: Plot of experimental viscosity $\eta_{\text{Exp.}}$ of binary mixtures of methane (1) + hexadecane (2) at $T = 373$ K against the molar volume V_m . *, $x_1 = 0$; □, $x_1 = 0.1013$; ◇, $x_1 = 0.2021$; △, $x_1 = 0.2976$ and ○, $x_1 = 0.3979$

Furthermore, the density and viscosity of the binary mixtures of CH_4 (1) + $\text{C}_{16}\text{H}_{34}$ (2) were correlated to enable interpolation of the results to any temperature and pressure condition within the range investigated. Again, density results were correlated by means of the modified Tait equation described in equations 7.1 through 7.3 and, the viscosity using the Tait-Andrade equation given in equations 7.5 to 7.7. Both correlations described our data very well and Figures 7.12 and 7.13 together with Tables 7.4 and 7.6 illustrate the quality of the correlations along with some statistical parameters for the various mole fractions of methane. The correlations were developed for each mole fraction of methane simply because for highly asymmetric systems (similar to those investigated in this work) there is no known good correlation (to the authors' knowledge) that relates either density or viscosity to mole fraction that can be used to reasonably describe the experimental data. The compositional-based correlations are used to give better description of the experimental results.

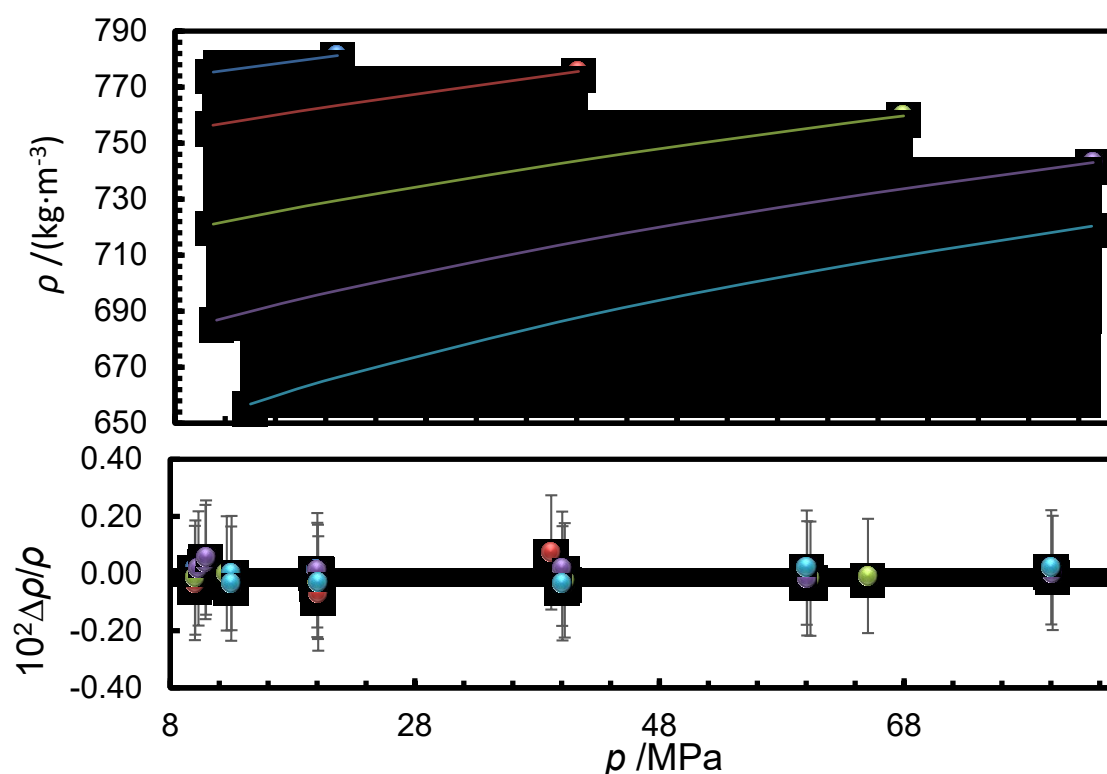


Figure 7.12: Experimental density ρ_{Exp} of binary mixture of $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$ at $x_1 = 0.2021$ as a function of pressure p / MPa: ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 373$ K; ●, $T = 423$ K and ●, $T = 473$ K. lines —, represent Tait correlation, equation 7.1

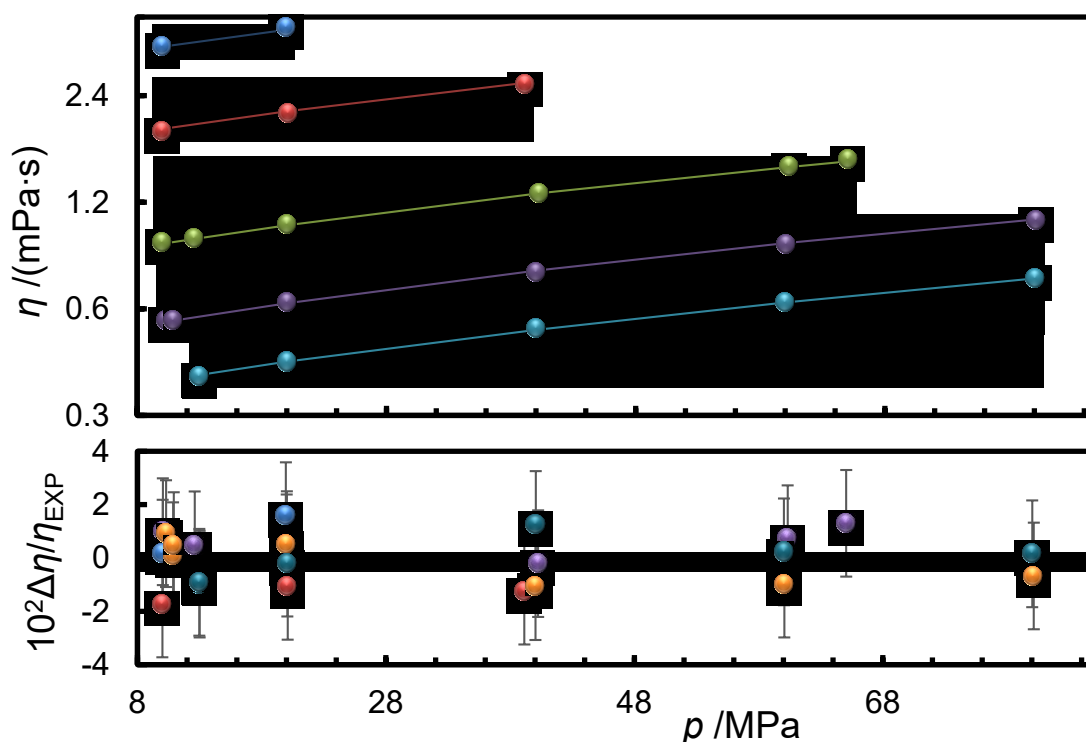


Figure 7.13: Experimental viscosity η_{Exp} of binary mixture of $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$ at $x_1 = 0.2021$ as function of pressure p / MPa: ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 373$ K; ●, $T = 423$ K and ●, $T = 473$ K. lines —, represent Tait-Andrade correlation, equation 7.5.

For this systems, there is no data available to compared with in the literature, so the experimental data along with the correlations developed in this work can be used as a basis for modelling the viscosity of the system.

7.6 Methane (1) + squalane (2)

The methane (1) + squalane (2) is the second binary system studied in this work. Again, the methane gas used was the research grade sourced from BOC gas ltd and the squalane was the analytical grade obtained from Sigma Aldrich UK with the stated mass purity of ($w = 99\%$). To verify the purity and also to identify the nature of the remaining 1 % impurities present, GC-MS analysis was carried out on the pure squalane sample using the column described in Table 7.7. Figures 7.14 and 7.15 show the chromatogram and the mass spectrum of the predominant impurities present in the sample respectively. From the chromatogram, an estimated mass purity of 98.7 % was deduced and the mass spectra of the impurities revealed that 2,6,10,14-tetramethylhexadecane was likely the predominant compound in the sample.

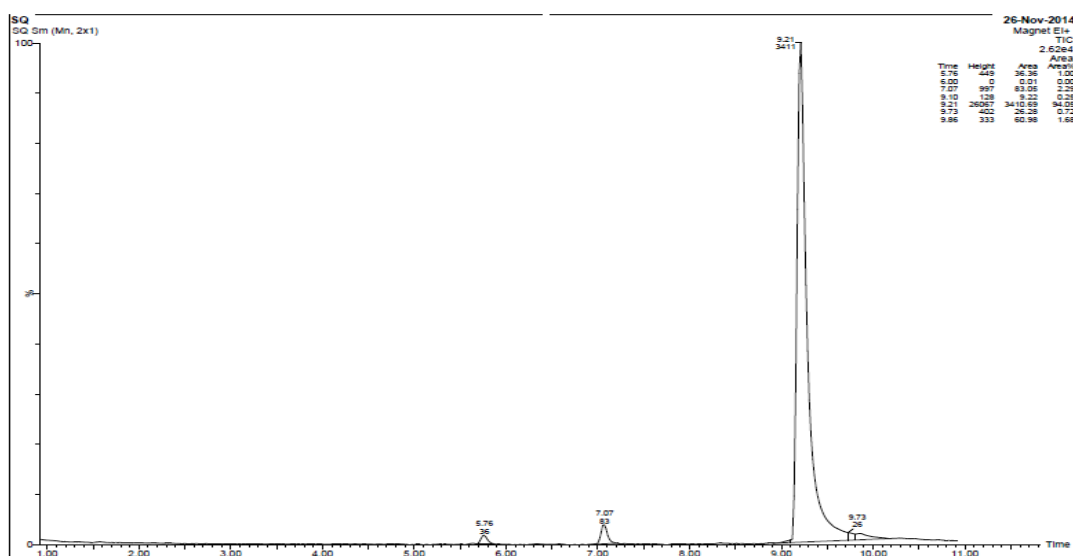


Figure 7.14: The chromatogram of the pure squalane sample

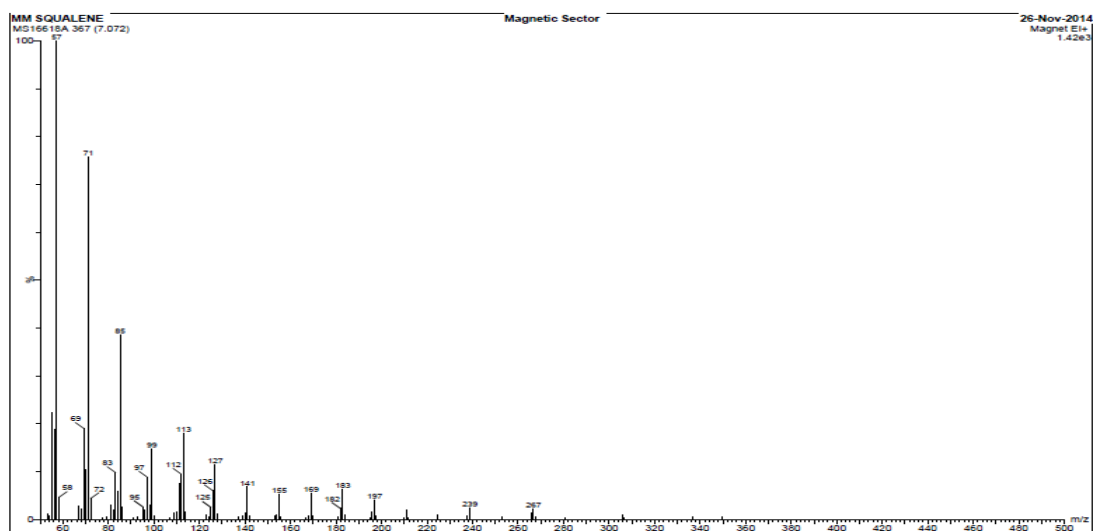


Figure 7.15: The mass spectrum of the dominant impurities present in the pure squalane

Viscosity and density of pure squalane have been published by Ciotta *et al.* [3, 24] previously in this laboratory and so, it was decided not to repeat this measurement and therefore, only the binary mixtures with methane were measured.

Vapour-liquid-equilibrium (VLE) data on this binary system were obtained from the work of Marteau *et al.*[25] in the temperature range (323 to 420) K and PR[1]-EoS was used to extend the data to $T = 473$ K after tuning the binary interaction parameters as shown in Figure 7.16.

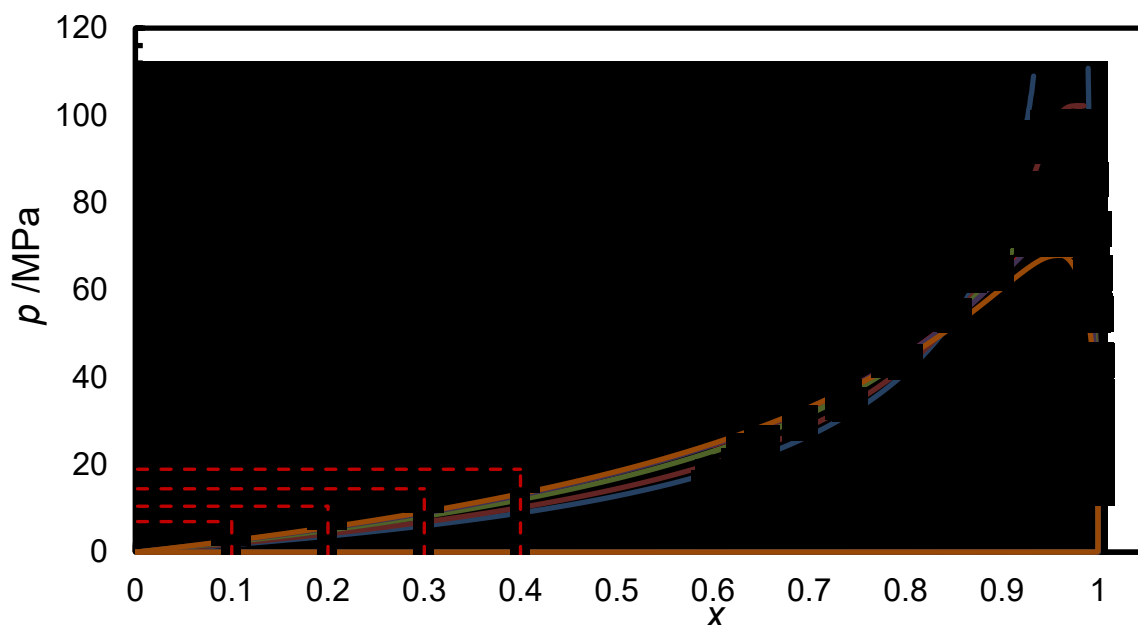


Figure 7.16: Phase diagram of CH_4 + squalane mixtures. Symbols represent literature data from Marteau *et al.*[25]. ●, $T = 323$ K; ●, $T = 370$ K; ●, $T = 420$ K; and lines —, represent Peng-Robinson^[1] equation of state in Aspen Hysys

Viscosity and density of the binary mixtures of CH₄ (1) + squalane (2) were simultaneously measured at four mole fractions of methane $x_1 = (0.1587, 0.2048, 0.3260$ and $0.4102)$ in the temperature range of (303 to 448) K and pressures up to 150 MPa. Table 7.14 shows the properties of the vibrating-wire used for these measurements. Tables B.6 to B.9 in appendix B present the results for this binary system whereas Figures 7.17 and 7.18 illustrate the results for both density and viscosity as functions of mole fractions of methane. A closer look at the figures revealed that the dissolution of methane reduced both the viscosity and density of squalane. However the decrease is more pronounced in viscosity compared to the effect on the density. Furthermore, it can also be deduced from the figures that the trends in both viscosity and density widens with increasing pressure as expected. Similarly, Figure 7.19 shows a plot of experimental viscosity as a function of molar volume of both pure squalane[24] and its mixtures with dissolved methane at $T = 398$ K.

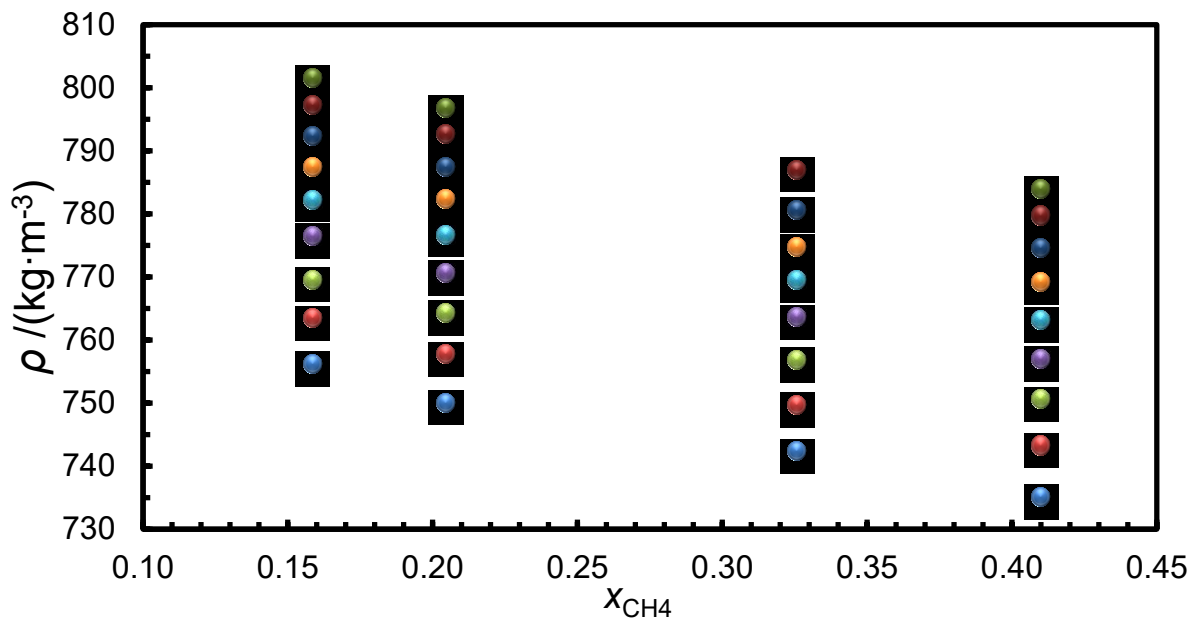


Figure 7.17: The experimental density $\rho_{Exp.}$ of binary mixtures of CH₄ + squalane as function of mole fraction of methane x at 398 K. ●, $p = 30$ MPa; ●, $p = 40$ MPa; ●, $p = 50$ MPa; ●, $p = 60$ MPa; ●, $p = 70$ MPa; ●, $p = 80$ MPa; ●, $p = 90$ MPa; ●, $p = 100$ MPa; ●, $p = 110$ MPa

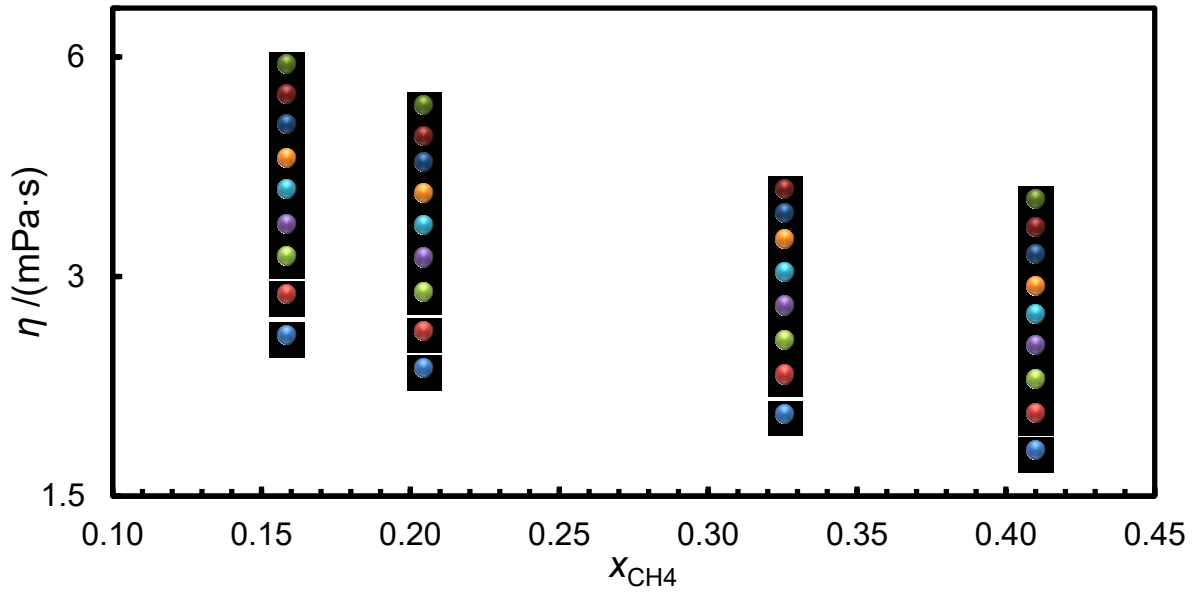


Figure 7.18: The experimental viscosity $\eta_{\text{Exp.}}$ of binary mixtures of CH_4 + squalane as function of mole fraction of methane x at 398 K. ●, $p = 30$ MPa; ●, $p = 40$ MPa; ●, $p = 50$ MPa; ●, $p = 60$ MPa; ●, $p = 70$ MPa; ●, $p = 80$ MPa; ●, $p = 90$ MPa; ●, $p = 100$ MPa; ●, $p = 110$ MPa

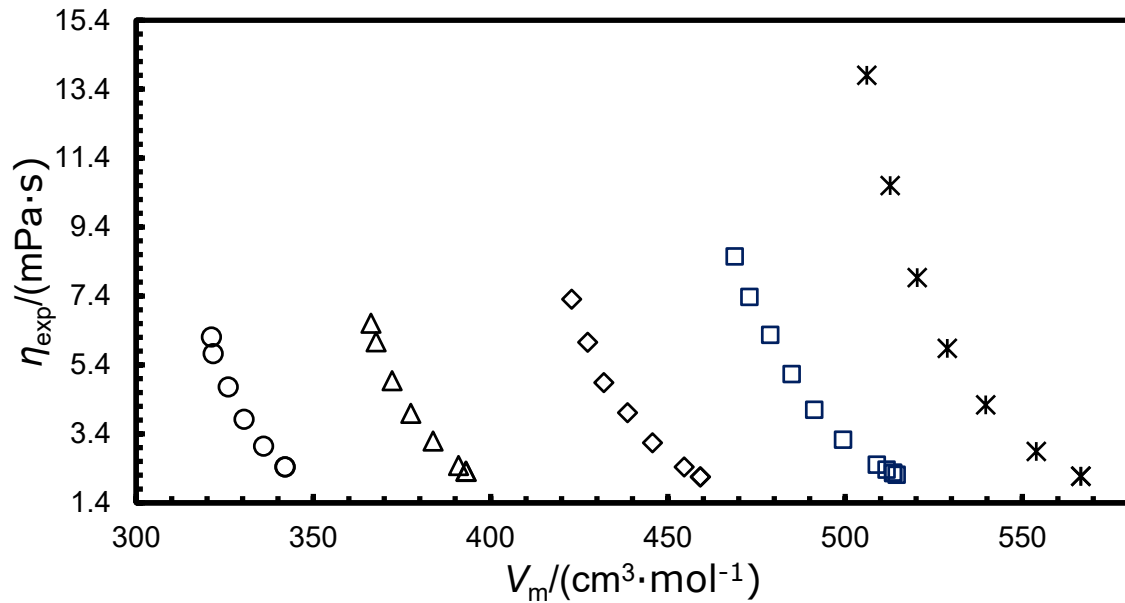


Figure 7.19: Plot of experimental viscosity $\eta_{\text{Exp.}}$ of binary mixtures of methane (1) + squalane (2) at $T = 398$ K against the molar volume V_m . *, $x_1 = 0$ from Ciotta *et al.*^[24]; □, $x_1 = 0.0950$; ◇, $x_1 = 0.1977$; △, $x_1 = 0.3143$ and ○, $x_1 = 0.4052$.

The results obtained were correlated using simple empirical relations that express both properties as functions of temperature and pressure. In order to allow for immediate comparison with other literature data, equations 7.1 and 7.5 were used to correlate the density and viscosity respectively. Figures 7.20 and 7.21 illustrate these correlations and their corresponding deviation plots of both density and viscosity for CH_4 (1) + squalane (2) at composition $x_1 = 0.3260$. It can be seen from the figures that these simple correlations

described most of our data within their expected uncertainties. The quality of the correlations and some statistical parameters are shown in Tables 7.8 and 7.9 for density and viscosity respectively for all the datasets. The slightly higher deviations observed when fitting the experimental viscosity suggest that, other empirical correlations that take density as an input (such as the extended hard-sphere model) could reduce the deviations and give more consistent results. This approach would however, limit the ability to compare the experimental results to only those literature sources where density data of the mixture is also available. For this system, to our knowledge there was no published literature data to compare with and hence, equations 7.1 and 7.5 along with Tables 7.8 and 7.9 provide useful correlations that could be used to estimate the viscosity and density of this system at any given state point within the range of temperature, pressure and composition investigated. Furthermore, these correlations could permit the extrapolations of both properties (density and viscosity) to other state points outside the range for which they were developed, however this should be applied with caution.

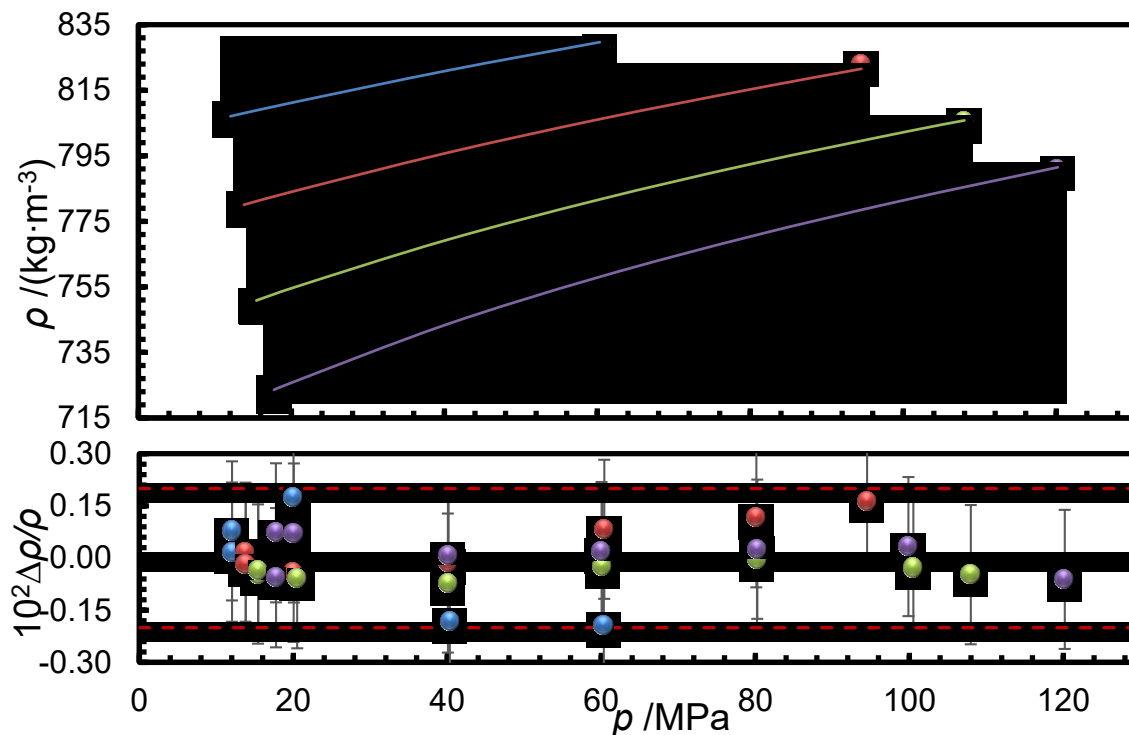


Figure 7.20: Experimental density ρ_{Exp} of binary mixture of CH_4 + squalane at $x_1 = 0.3260$ as function of pressure p /MPa. ●, $T = 303$ K; ●, $T = 348$ K; ●, $T = 398$ K; ●, $T = 448$ K and lines —, represent Tait correlation, equation 7.1

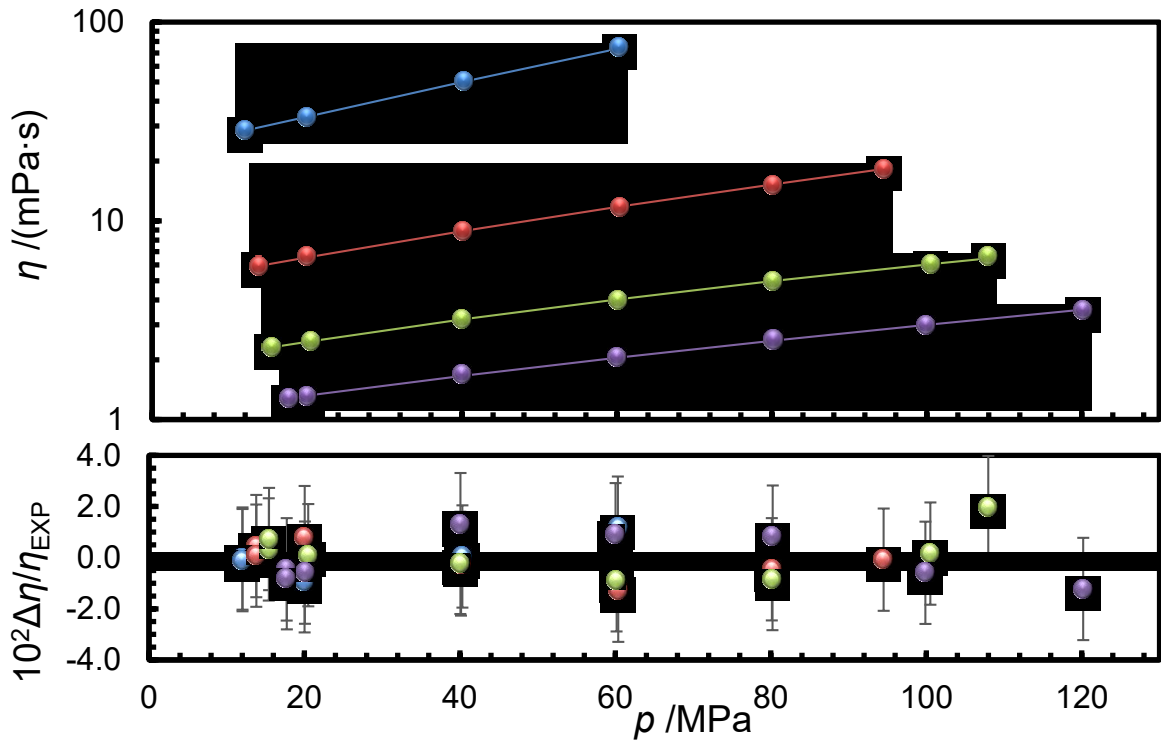


Figure 7.21: Experimental viscosity η_{Exp} of binary mixture of CH_4 + squalane at $x_1 = 0.3260$ as function of pressure p /MPa. ●, $T = 303$ K; ●, $T = 348$ K; ●, $T = 398$ K; ●, $T = 448$ K and lines —, represent Tait-Andrade correlation, equation 7.5.

Table 7.8: Statistical Parameters for the Density Correlation of $x\text{CH}_4$ (1) + Squalane (2) Mixtures at Different Compositions and Coefficients of Equations (7.1, 7.2 and 7.3)

Coefficient	$x_1 = 0.1587$	$x_1 = 0.2048$	$x_1 = 0.3260$	$x_1 = 0.4102$
C	2.33×10^{-1}	2.09×10^{-1}	2.01×10^{-1}	1.90×10^{-1}
a_0	3.76×10^2	2.71×10^2	4.88×10^2	7.45×10^2
a_1	-2.79×10^2	-1.73×10^2	-4.57×10^2	-7.85×10^2
a_2	5.27×10^1	2.34×10^1	1.15×10^2	2.16×10^2
b_0	1.00×10^3	1.00×10^3	9.98×10^2	9.32×10^2
sb_1	-1.86×10^2	-1.89×10^2	-1.74×10^2	-6.84×10^1
b_2	2.81×10^0	3.54×10^0	-3.45×10^1	-4.52×10^1
$10^2 \Delta_{\text{AAD},p}$	0.10	0.06	0.06	0.19
$10^2 \Delta_{\text{MAD},p}$	0.44	0.24	0.19	0.59
$10^2 \Delta_{\text{bias},p}$	0.00	0.00	0.00	0.00

Table 7.9: Statistical Parameters for the Viscosity Correlation of $x\text{CH}_4$ (1) + Squalane (2) Mixtures at Different Compositions and Coefficients of Equations (7.5, 7.6 and 7.7)

Coefficient	$x_1 = 0.1587$	$x_1 = 0.2048$	$x_1 = 0.3260$	$x_1 = 0.4102$
A_η	7.56×10^{-2}	8.17×10^{-2}	9.01×10^{-2}	1.04×10^{-1}
B_η	6.99×10^2	6.55×10^2	6.31×10^2	5.87×10^2
C_η	-1.81×10^2	-1.87×10^2	-1.89×10^2	-1.93×10^2
d_0	1.90×10^1	5.71×10^1	5.37×10^1	5.47×10^1
d_1	-5.69×10^1	-1.75×10^2	-1.53×10^2	-1.45×10^2
d_2	4.75×10^1	1.38×10^2	1.14×10^2	1.01×10^2
e_0	1.70×10^3	5.78×10^3	4.16×10^3	3.43×10^3
e_1	-1.93×10^3	-7.24×10^3	-5.50×10^3	-4.85×10^3
e_2	5.98×10^2	2.31×10^3	1.88×10^3	1.81×10^3
$10^2 \Delta_{\text{AAD}, \eta}$	0.70	0.86	0.63	0.82
$10^2 \Delta_{\text{MAD}, \eta}$	2.68	3.03	1.98	3.46
$10^2 \Delta_{\text{bias}, \eta}$	0.01	0.01	0.01	0.01

7.7 Methane (1) + cyclohexane (2) - $[x\text{CH}_4 + (1-x) \text{C}_6\text{H}_{12}]$

The viscosity and density of binary mixtures of cyclohexane with dissolved methane were measured as part of this work. The cyclohexane with a claimed percentage mass purity $w > 99.5\%$ was obtained from Sigma Aldrich UK. Again, no additional purification was conducted, but nonetheless, a GC-MS analysis was carried out on the pure cyclohexane sample with the view to verify its purity and also to identify the possible impurities present. Table 7.7 describes the properties of the column employed for this analysis, and Figures 7.22 and 7.23 the chromatogram as well as the mass spectrum of the dominant impurity. An estimated percentage mass purity of $w = 99.8\%$ was deduced from Figure 7.22, whereas Figure 7.23 revealed that the dominant impurity present is likely methylcyclohexane.



Figure 7.22: The chromatogram of the pure cyclohexane sample

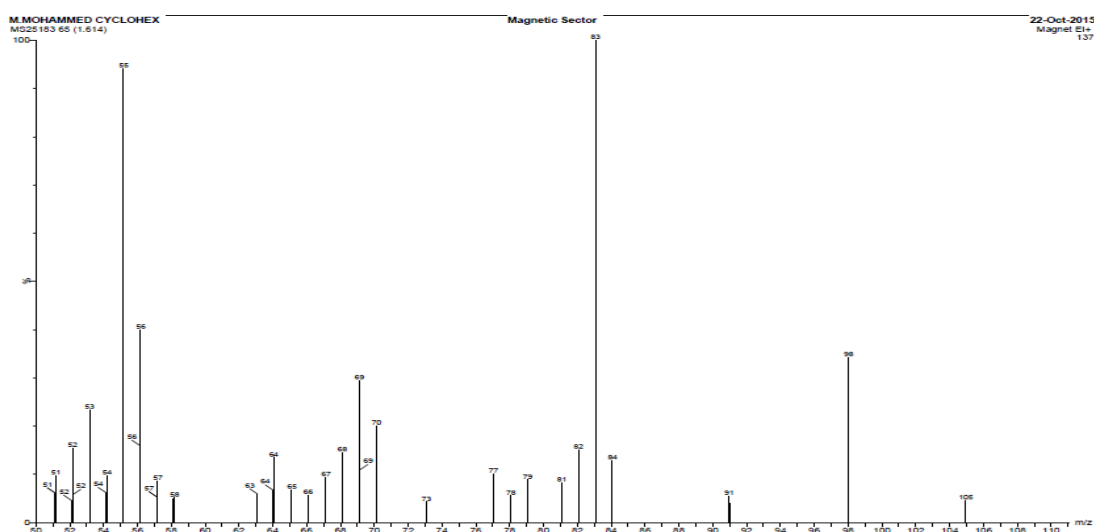


Figure 7.23: The mass spectrum of the dominant impurities present in the pure cyclohexane

Prior to the preparation of the mixture, VLE data on the binary mixtures of cyclohexane with dissolved methane was obtained from Reamer *et al.*[26] in the literature and PR[1]-EoS was used after tuning the binary interaction parameter to extend the data to the desired upper limit temperature isotherm (473 K) as shown in Figure 7.24.

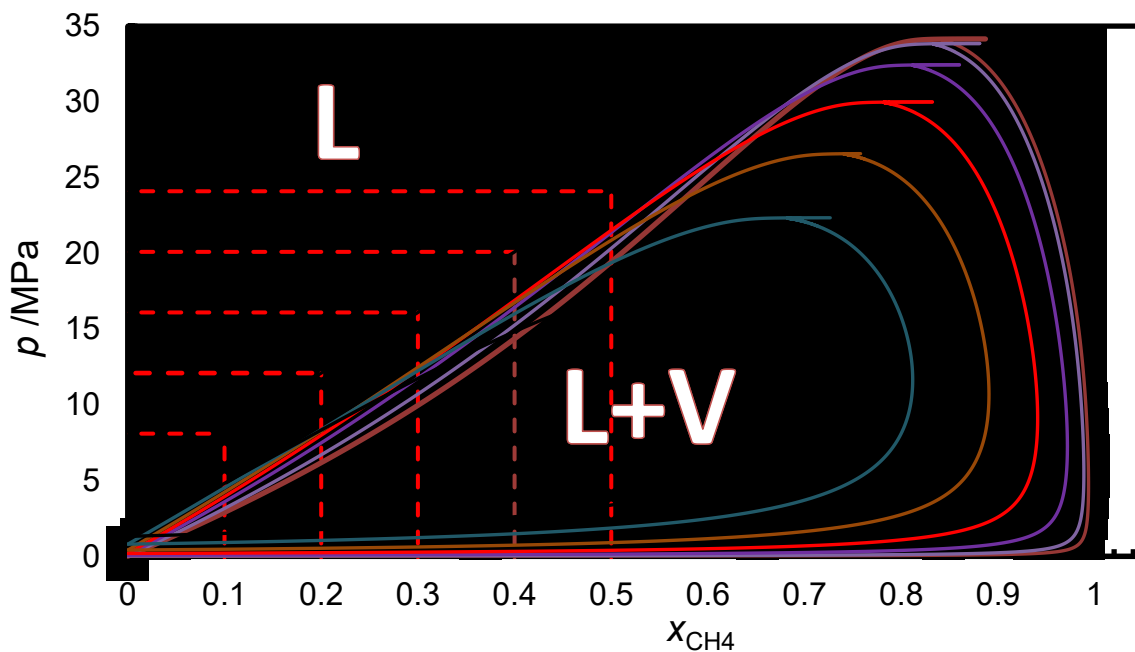


Figure 7.24: Phase diagram of CH₄ + cyclohexane mixtures. Symbols represent literature data from Reamer *et al.*^[26] ●, $T = 294$ K; ●, $T = 310$ K; ●, $T = 344$ K; ●, $T = 377$ K; ●, $T = 410$ K; ●, $T = 444$ K and —, $T = 473$ K. All lines represent Peng-Robinson^[1] equation of state in Aspen Hysys

The viscosity and density of pure cyclohexane and its binary mixtures with dissolved methane have been measured simultaneously at five different mole fractions of methane $x = (0, 0.0992, 0.2073, 0.3031 \text{ and } 0.4020)$. As viscosity and density of pure cyclohexane have been extensively reported in the literature, only few data points were measured in this work for re-validation purposes. For the pure cyclohexane, measurements were conducted at temperatures (298, 323, 348 and 423) K and pressures up to 60 MPa. For the binary mixtures however, measurements were made in the temperature range (298 to 473) and pressures generally up to 200 MPa. The viscosity and density measurements were carried out using the VWVD device that was re-commissioned as part of this work operated in absolute mode with the properties shown in Table 7.14. Figure 7.25 illustrates a plot of experimental viscosity as a function of molar volume at $T = 323$ K while Tables B.10 to B.14 in appendix B present the results with the experimental temperatures given in the tables slightly differed from the nominal values but were constant to ± 0.02 K for a given isotherm.

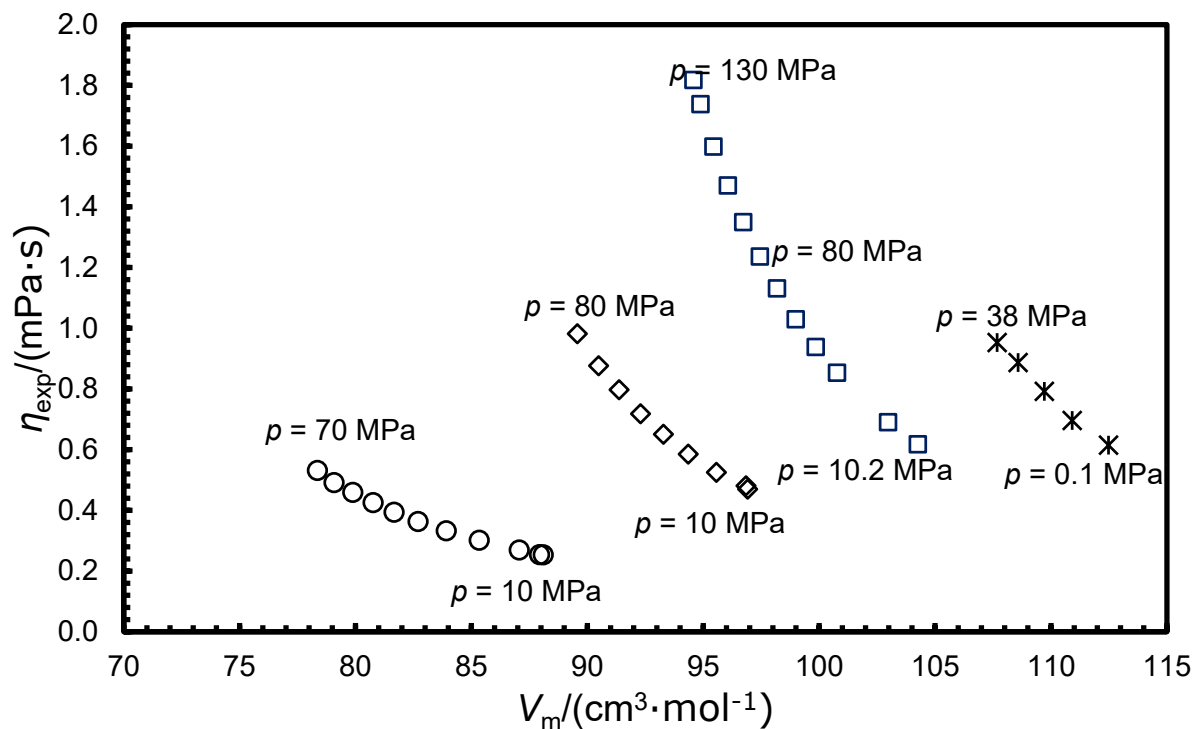


Figure 7.25: Plot of experimental viscosity $\eta_{\text{Exp.}}$ of binary mixtures of methane (1) + cyclohexane (2) at $T = 323$ K against the molar volume V_m . *, $x_1 = 0$; $\square$, $x_1 = 0.0992$; $\diamond$, $x_1 = 0.2073$; $\triangle$, and $\circ$, $x_1 = 0.4020$

The experimental results were correlated both for density and viscosity using simple empirical expressions that take temperature and pressure as independent parameters in order to permit immediate comparison of our results with the available data in the literature. The modified Tait equation and the Tait-Andrade equation presented in section 7.3 were used to correlate the experimental density and viscosity of both pure cyclohexane and its binary mixtures with dissolved methane. Figures 7.26 and 7.27 illustrate these correlations both of which relate to the mixture of cyclohexane with dissolved methane at composition $x = 0.3031$.

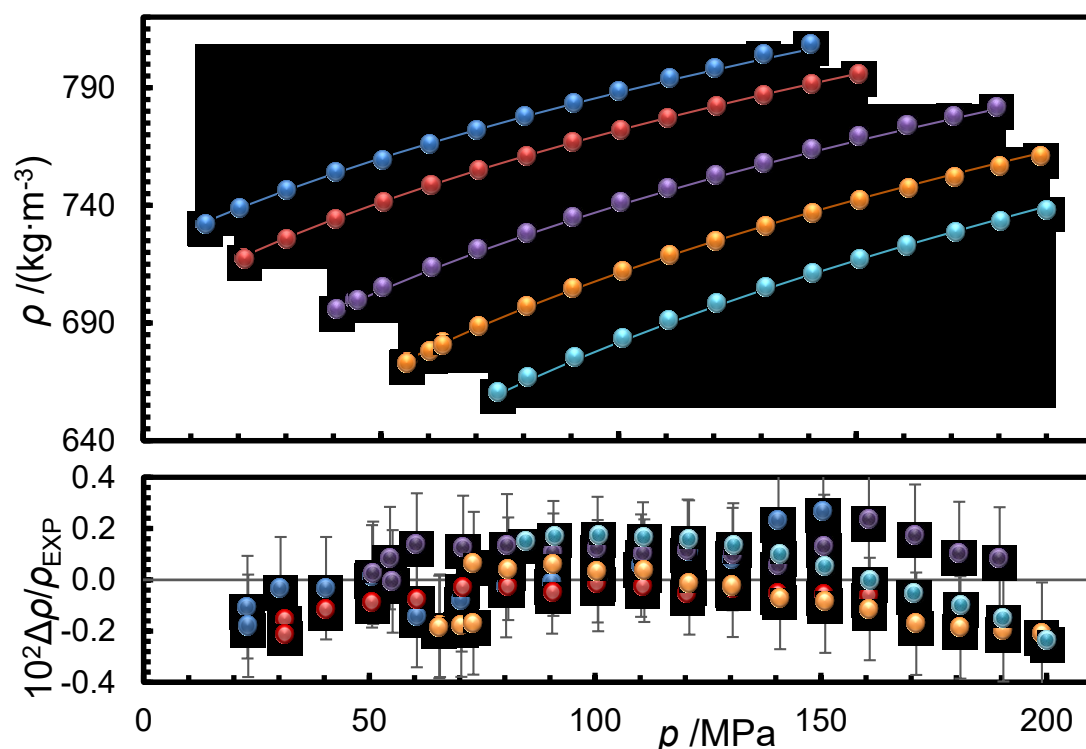


Figure 7.26: Experimental density ρ_{Exp} of binary mixture of $\text{CH}_4 + \text{cyclohexane}$ at $x_1 = 0.3031$ as function of pressure p / MPa . $\bullet$, $T = 298 \text{ K}$; $\bullet$, $T = 323 \text{ K}$; $\bullet$, $T = 373 \text{ K}$; $\bullet$, $T = 423 \text{ K}$; $\bullet$, $T = 473 \text{ K}$ and lines —, represent Tait correlation, equation 7.1

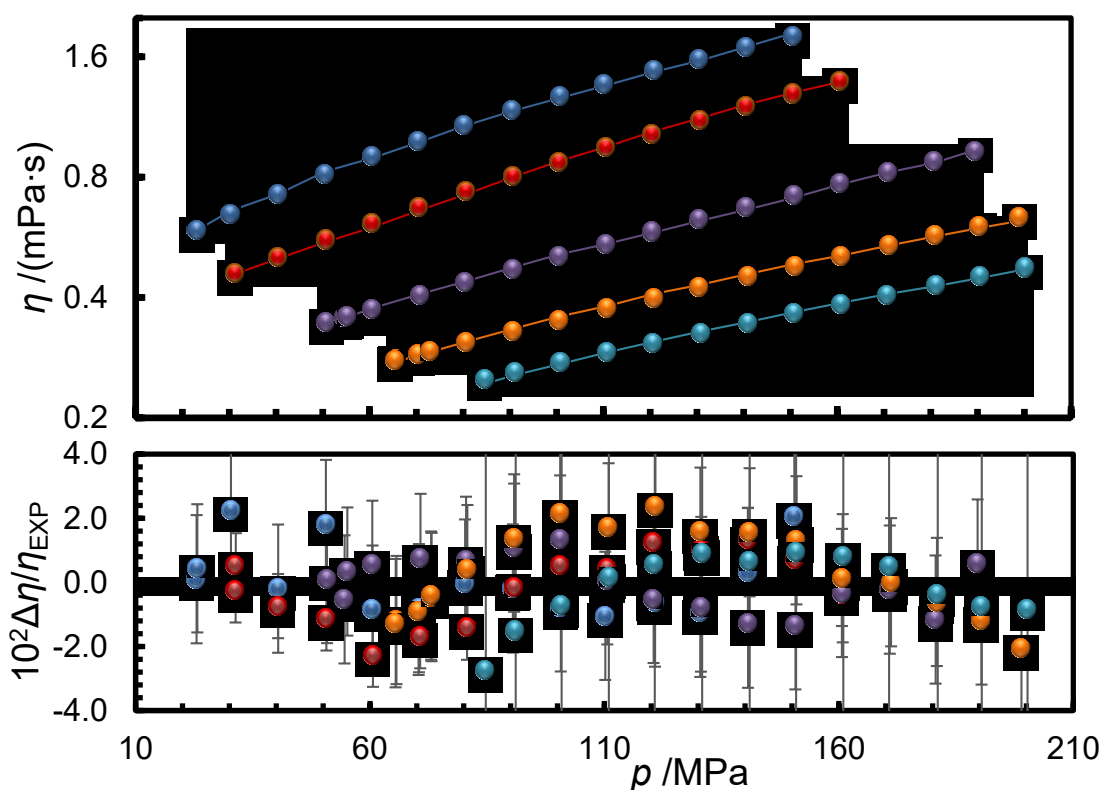


Figure 7.27: Experimental viscosity η_{Exp} of binary mixture of $\text{CH}_4 + \text{cyclohexane}$ at $x_1 = 0.3031$ as function of pressure p / MPa . $\bullet$, $T = 298 \text{ K}$; $\bullet$, $T = 323 \text{ K}$; $\bullet$, $T = 373 \text{ K}$; $\bullet$, $T = 423 \text{ K}$; $\bullet$, $T = 473 \text{ K}$ and lines —, represent Tait-Andrade correlation, equation 7.5.

As can be seen from the deviations plots, these simple correlations described our data very well as most of the deviations fell within the estimated uncertainty of the equations. Moreover, Tables 7.10 and 7.11 present the coefficients of the equations and also highlight the quality of these correlations for the rest of the data.

Table 7.10: Statistical Parameters for the Density Correlation of CH₄ (1) + cyclohexane (2) Mixtures at Different Compositions and Coefficients of Equations (7.1, 7.2 and 7.3)

Coefficient	$x_1 = 0$	$x_1 = 0.0992$	$x_1 = 0.2073$	$x_1 = 0.3031$	$x_1 = 0.4020$
C	2.64×10^{-1}	1.99×10^{-1}	2.16×10^{-1}	2.28×10^{-1}	2.14×10^{-1}
a_0	1.10×10^3	1.23×10^3	9.41×10^2	8.87×10^2	4.02×10^2
a_1	-3.39×10^2	-5.41×10^2	-8.69×10^1	-4.93×10^1	6.74×10^2
a_2	3.28×10^1	1.03×10^2	-9.01×10^1	-1.03×10^2	-4.18×10^2
b_0	5.66×10^2	2.91×10^2	3.51×10^2	3.51×10^2	2.41×10^2
b_1	-6.31×10^2	-2.86×10^2	-3.70×10^2	-3.70×10^2	-2.77×10^2
b_2	1.91×10^2	7.08×10^1	9.87×10^1	9.87×10^1	7.98×10^1
$10^2 \Delta_{\text{AAD}, \rho}$	0.02	0.06	0.07	0.10	0.10
$10^2 \Delta_{\text{MAD}, \rho}$	0.05	0.22	0.23	0.27	0.28
$10^2 \Delta_{\text{bias}, \rho}$	0.00	0.00	0.01	0.00	-0.01

Table 7.11: Statistical Parameters for the Viscosity Correlation of CH₄ (1) + cyclohexane (2) Mixtures at Different Compositions and Coefficients of Equations (7.5, 7.6 and 7.7)

Coefficient	$x_1 = 0$	$x_1 = 0.0992$	$x_1 = 0.2073$	$x_1 = 0.3031$	$x_1 = 0.4020$
A_η	4.74×10^{-3}	3.33×10^{-2}	3.32×10^{-3}	4.58×10^{-2}	1.67×10^{-8}
B_η	1.69×10^3	5.40×10^2	1.87×10^3	4.36×10^2	2.62×10^4
C_η	2.40×10^1	-1.30×10^2	6.23×10^1	-1.01×10^2	1.28×10^3
d_0	2.12×10^1	7.42×10^0	5.76×10^{-1}	-1.24×10^1	5.43×10^{-1}
d_1	-5.56×10^1	-2.28×10^1	-1.13×10^0	5.64×10^1	-4.11×10^{-1}
d_2	3.79×10^1	1.99×10^1	3.70×10^0	-4.50×10^1	1.45×10^0
e_0	2.17×10^3	2.85×10^3	8.47×10^2	-4.14×10^3	5.07×10^2
e_1	-3.04×10^3	-3.73×10^3	-7.92×10^2	5.63×10^3	-5.09×10^2
e_2	1.08×10^3	1.26×10^3	1.97×10^2	-1.61×10^3	1.32×10^2
$10^2 \Delta_{\text{AAD}, \eta}$	0.3	0.65	0.88	1.09	2.11
$10^2 \Delta_{\text{MAD}, \eta}$	0.96	2.59	2.45	2.74	3.41
$10^2 \Delta_{\text{bias}, \eta}$	0.01	0.01	0.01	0.01	0.03

7.7.1 Comparison with available literature data

Extensive data on the viscosity and density of pure cyclohexane are readily available for comparison in the literature. For convenience, only high-pressure datasets were selected

and compared with our results. For density, datasets from references^[9, 12, 22, 27-37] were chosen and then compared with equation 7.1 as shown in Figure 7.28.

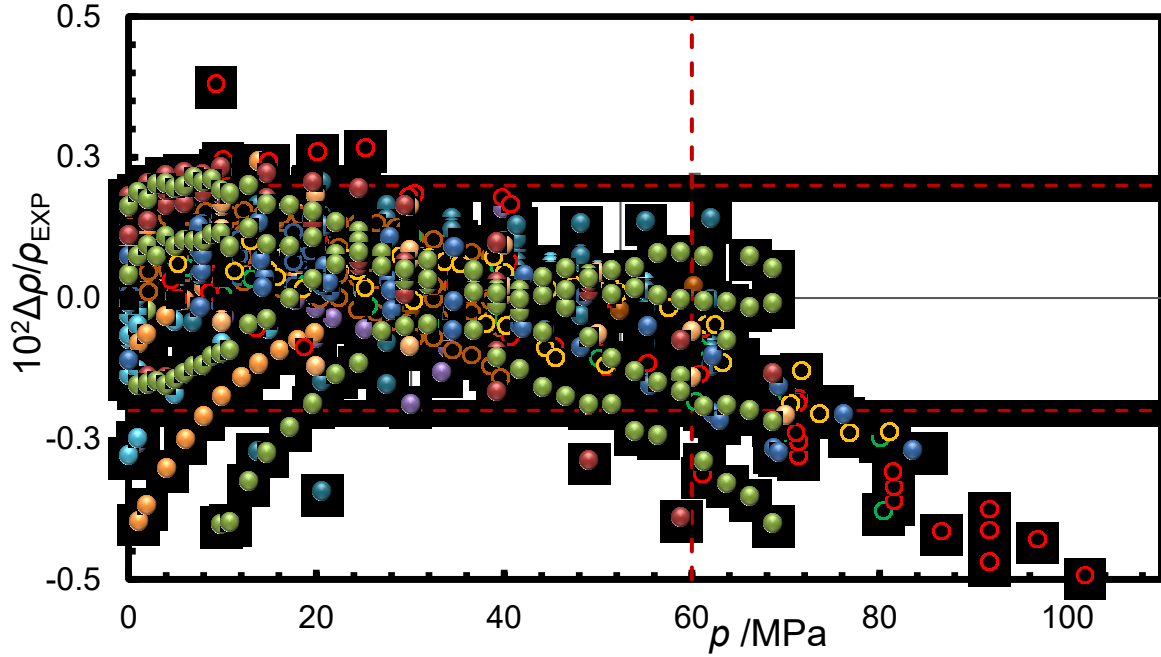


Figure 7.28: Fractional deviation of density of pure cyclohexane from equation 7.1 as a function of pressure p : ●, This work; ●, Vega-Maza *et al.*^[28]; ●, Berstad^[27]; ●, Davila *et al.*^[29]; ●, sommer *et al.*^[30]; ●, Zhou *et al.*^[31]; ●, Amorim *et al.*^[12]; ●, Moravkova *et al.*^[22]; ●, Wang *et al.*^[32]; ●, Tanaka *et al.*^[9]; ●, Toscani *et al.*^[33]; ○, Sun *et al.*^[34]; ●, Li *et al.*^[35]; ○, Kashiwagi *et al.*^[36]; and ---, maximum pressure $p_{\max.} \leq 60$ MPa limit at which equation 7.1 is valid.

As seen in Figure 7.28 and Table 7.12 most of the literature data agree very well with our correlation with less than 5 % of all the data considered fall outside the expanded uncertainty of 0.3 % of our measurements. Furthermore, most of the higher deviations observed occurred at higher pressures close to the freezing pressures of the pure cyclohexane at the corresponding temperatures.

Table 7.12: Deviations of the literature density data for cyclohexane from equation 7.1

Source	$10^2 \Delta_{\text{AAD},p}$	$10^2 \Delta_{\text{bias},p}$	$10^2 \Delta_{\text{MAD},p}$
This Work	0.02	0.00	0.05
Berstad ^[27] 1989	0.06	0.00	0.26
Vega-Maza, <i>et al.</i> ^[28] 2013	0.07	0.09	0.16
Davila, <i>et al.</i> ^[29] 2011	0.05	0.02	0.28
Sommer <i>et al.</i> ^[30] 2011	0.10	0.03	0.40
Zhou <i>et al.</i> ^[31] 2010	0.04	0.09	0.18
Amorim <i>et al.</i> ^[12] 2007	0.09	0.04	0.34
Moravkova <i>et al.</i> ^[22] 2007	0.07	0.05	0.15

Wang <i>et al.</i> ^[32] 1996	0.03	0.08	0.23
Tanaka <i>et al.</i> ^[9] 1991	0.10	0.04	0.38
Toscani <i>et al.</i> ^[33] 1990	0.18	-0.05	0.49
Sun <i>et al.</i> ^[34] 1987	0.08	0.04	0.27
Li <i>et al.</i> ^[35] 1984	0.08	-0.02	0.24
Kashiwagi <i>et al.</i> ^[36] 1982	0.08	0.04	0.21
Jonas <i>et al.</i> ^[38] 1980	0.54	-0.20	0.54
Kashiwagi <i>et al.</i> ^[39] 1982b	0.08	0.04	0.14
Kashiwagi <i>et al.</i> ^[40] 1979	0.14	0.05	0.52
Apaev <i>et al.</i> ^[37] 1972	0.14	0.04	0.52
Kerimov <i>et al.</i> ^[37] 1972	0.12	-0.12	0.40

Similarly for viscosity of pure cyclohexane, a large body of high-pressure datasets[9, 27, 38, 41-46] were gathered from the literature. Tariq *et al.*[47] critically analysed most of these datasets and categorised them as primary and secondary datasets. For the sake of comparison with our correlations, only the primary datasets will considered here. Figure 7.29 illustrates a comparison of some primary datasets and our correlating equation 7.7.

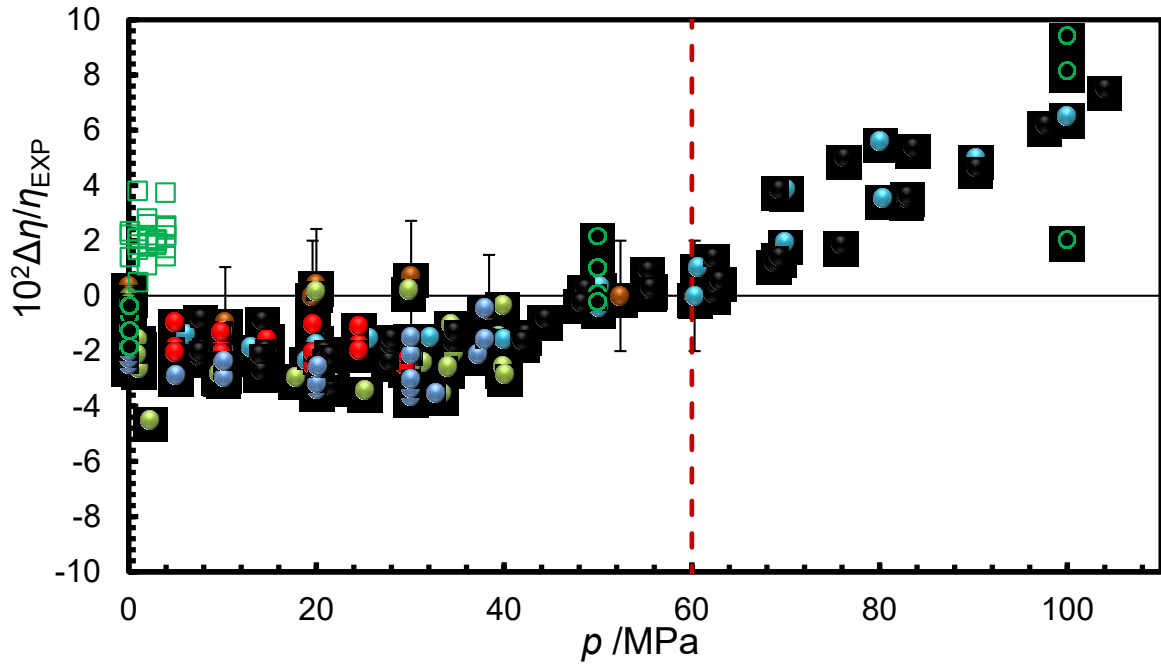


Figure 7.29: Fractional deviation of viscosity of pure cyclohexane from equation 7.5 as a function of pressure p : ●, This work; ●, Berstad^[27]; ●, Tanaka *et al.*^[9]; ●, Knapstad *et al.*^[42]; ●, Gonzalez *et al.*^[43]; ●, Kashiwagi and Makita.^[36]; ●, Padua *et al.*^[44]; ○, Isdale *et al.*^[48]; □, Liu *et al.*^[49]; and ---, maximum pressure $p_{\max.} \leq 60$ MPa limit at which equation 7.5 is valid.

From Figure 7.29 it is evident that most of the primary datasets considered in the plot agree well with our results within the mutual uncertainties of our measurements and those of the reference concerned. For instance, most of the data from Berstad [27]; Knapstad *et al.*[42]; Padua *et al.*[44] and Gonzalez *et al.*[43] all agree with our results to within ± 2 % in the validity range (i.e. maximum pressure $p_{\max.} \leq 60$ MPa) of the equation with few outliers. However, some systematic deviations were observed at pressures higher than $p_{\max.} \leq 60$ MPa as can be seen from the datasets of Kashiwagi and Makita.[36], Tanaka *et al.*[9] and Isdale *et al.*[48]. Table 7.13 summarises the deviations of these datasets from the correlating equation 7.5.

Table 7.13: Deviations of the Literature Viscosity Data for Cyclohexane from Equation 7.5

Source	$10^2 \Delta_{\text{AAD}, \eta}$	$10^2 \Delta_{\text{bias}, \eta}$	$10^2 \Delta_{\text{MAD}, \eta}$
This Work	0.3	0.0	0.7
Berstad ^[27] 1989	0.8	-2.2	4.5
Tanaka, <i>et al.</i> ^[9] 1991	2.2	-0.0	6.5
Knapstad, <i>et al.</i> ^[42] 1989	0.4	-1.0	1.7
Gonzalez <i>et al.</i> ^[43] 2007	0.4	-1.8	2.5
Kashiwagi, and Makita. ^[36] 1982	2.1	-0.1	9.4
Padua, <i>et al.</i> ^[44] 1996	0.6	-2.5	3.6
Hernandez, <i>et al.</i> ^[45] 2009	3.6	-3.9	12.3
Liu <i>et al.</i> ^[49] 2015	0.5	-2.1	3.8
Isdale, <i>et al.</i> ^[48] 1979	3.2	2.2	9.4

Furthermore, our viscosity results for the pure along with some other literature data cyclohexane have been compared with a published reference correlation from Tariq *et al.*^[47] as shown in Figure 7.30. This correlation described our data with average absolute deviation Δ_{AAD} of 2.8 % and maximum absolute deviation of Δ_{MAD} of 3.9 %. However, it was observed that the correlation slightly under-predicted our experimental data from the negative bias obtained. In comparison with other literature sources, the correlation reproduced the experimental data from Berstad[27], Padua *et al.*[44], Tanaka *et al.*[9] and Jonas *et al.*[38]. with Δ_{AAD} 's of 1.8 %, 0.8 %, 0.7 % and 4.2 % and with Δ_{MAD} 's of 3.5 %, 1.9 %, 1.8 % and 11.8 % respectively. It is important to note that the comparison was limited to the literature sources in which both density and viscosity data were provided, as the correlation requires density input.

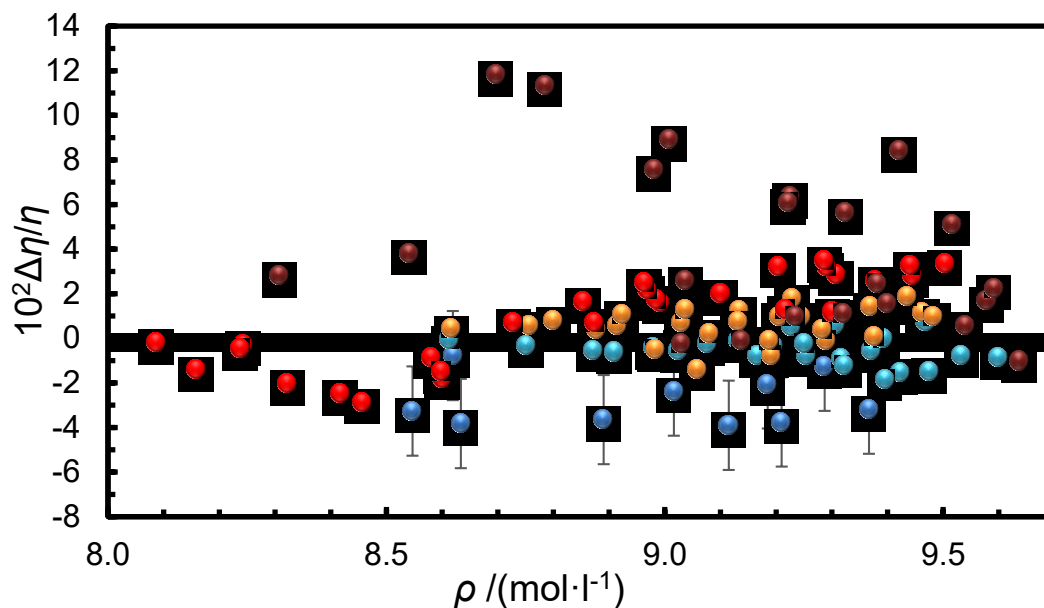


Figure 7.30: Fractional deviation of viscosity of pure cyclohexane from reference correlation of Tariq *et al.*^[47] as a function of density ρ : ●, this work; ●, Berstad^[27]; ●, Padua *et al.*^[44]; ●, Tanaka *et al.*^[9]; ●, Jonas *et al.*^[38] —, viscosity correlation from Tariq *et al.*^[47]

It can be seen from Table 7.30 that the data from this work were slightly lower than those reported in the literature as well as the reference correlation. However, looking closely at the figure, it can be seen that only few data points were measured in this work (see Table B.20 in appendix B) only for validation purposes as the viscosity of pure cyclohexane has been well-studied in the literature. Furthermore, taking into account the mutual uncertainties of our measurement (2 % as indicated by the error bars) and those of the reported literature sources concerned as well as that of the correlation (could be up to 5 % at high pressure, high temperature), it can be said that our data are comparable with most of the datasets shown in Figure 7.30.

7.7.2 Comparison with literature data of mixtures of cyclohexane with dissolved methane

To the author's knowledge, only one previous datasets by Berstad^[27] on the viscosity and density of binary mixtures of cyclohexane with dissolved methane was available in the literature. This author measured the viscosity and density of binary mixtures of cyclohexane + methane at three different mole fractions $x = (0.230, 0.407 \text{ and } 0.565)$ of methane. The datasets were gathered in the ranges of temperature (295 to 443) K and pressure (10 to 40) MPa. These datasets were compared with the present work for the two methane mole fractions in the range investigated in this work. Figure 7.29 illustrate these comparisons for methane mole fractions $x = 0.230$ and $x = 0.407$ along 323 K

isotherm. However, it is important to note that the compositions of the mixture as well as the temperature and pressure measured by Berstad[27] slightly differed from the ones investigated in this work. For instance, while the present work measured the viscosity and density of the mixtures at methane mole fractions x ($= 0, 0.0992, 0.2073, 0.3031$ and 0.4020), Berstad[27] investigated in the composition range highlighted above. Therefore plots like Figure 7.30 will only serve as a qualitative means of comparing and interpolating between the two datasets.

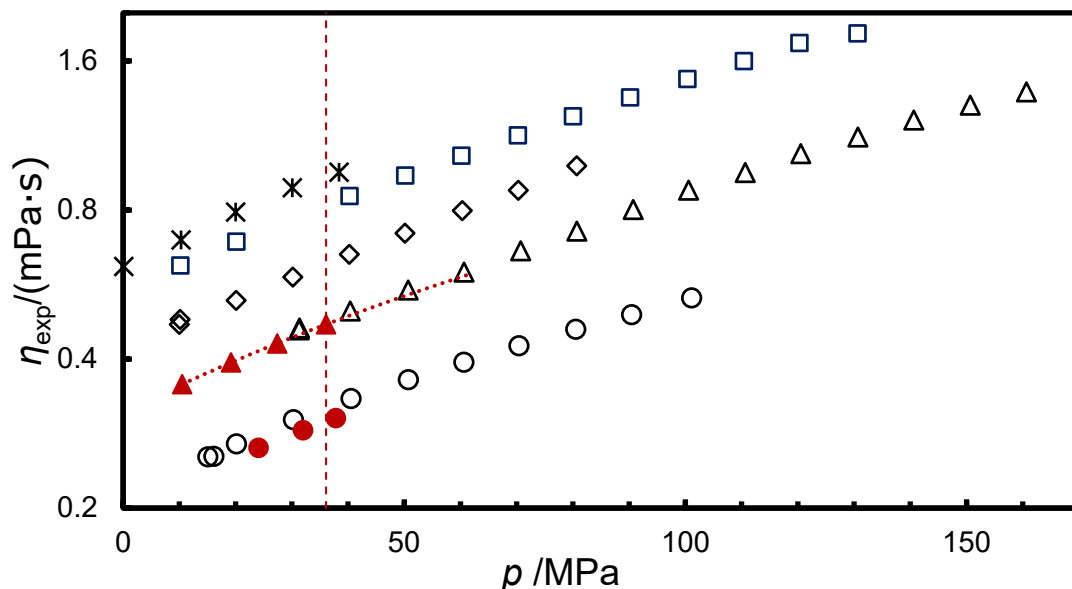


Figure 7.31: Comparison between experimental viscosity results of this work and datasets obtained from Berstad^[27] as a function of pressure p . Open blue symbols represent This work at 323 K: *, at $x = 0$; □, at $x = 0.0992$; ◇, at $x = 0.2073$; △, at $x = 0.3031$ and ○, at $x = 0.4020$, and Filled red symbols represent Berstad ^[27] data: , at ▲, $x = 0.230$ and $T = 324$ K; and ●, at $x = 0.4070$ and $T = 326$ K

From Figure 7.31, it can be seen that our results are in agreement with the datasets from [27]. This is evident from the fact that our datasets for the mole fraction of methane $x = 0.2073$ aligned very well with the datasets from Berstad[27] at $x = 0.230$. Furthermore, it can be observed that the viscosity values from Berstad[27] at mole fraction $x = 0.4070$ are slightly lower than the values obtained in the present work, this can be explained by the slight temperature differences (i.e. $\Delta T = 3$ K) between the two datasets..

7.8 Perfluoropolyether (Krytox® oil GPL 102)

Perfluoropolyethers belong to the class of synthetic oils used in many high-temperature lubricants and hydraulic fluid applications[50-52]. Krytox® belongs to the perfluoropolyether group of compounds and it is a trademarked name of a family of high performance lubricants containing ether functionality. It is a series of low molecular-weight fluorinated

oils that typically contains about 21.6 % carbon, 9.4 % oxygen and 69.0 % fluorine by weight composition[53]. Krytox®'s excellent physical, chemical and environmental properties make them attractive for many applications. Some of these properties includes; good thermal stability, chemical inertness, low vapour pressure, low surface energy, nontoxic, non-flammable and environmentally benign[54].

Krytox® can be synthesised in a wide range of viscosity as oil or grease depending on the intended application, as such, over 100 different grades and series of krytox® are available. For instance, the GPL 10X series, where X ranges from 0 to 7 are commonly used in industries such as: chemical, pharmaceutical, plastic, textile, refrigeration industries etc. Krytox® GPL102 with general formula $F-(CF(CF_3)CF_2O)_n-CF_2CF_3$, $n \approx 9.528$ and with number average molecular weight $M = 1720$ (g/mol) is the candidate of interest in this study.

The International Association for Transport properties (IATP) at her 9th regular meeting in 2009 held at Boulder Colorado USA, has identified the need to find a new high-pressure, high-temperature viscosity standard to represent the low viscosity crude oil found in very deep offshore wells in the Gulf of Mexico. The new candidate should have a target viscosity of about 20 mPa·s at 473 K and 200 MPa and should have the following properties: it should be chemically and thermally stable at extreme conditions: it should be non-toxic, non-flammable and environmentally inert and also should be widely available in high purity. Based on the considerations of the above properties, krytox® GPL 102 series was proposed as a potential candidate. However, the viscosity of krytox® has not been widely studied in the past and to that effect, the National Energy Technology Laboratory procured large volume of krytox® GPL 102, LOT K2391 and distributed portions to some laboratories for high-pressure viscosity measurements. Our Laboratory is one of the recipients of the product and our vibrating-wire viscometer can measure up to the desired temperature and pressure ranges.

However, due to the high-density and high-viscosity nature of krytox® oil and coupled with the fact that this will be the first time we are putting highly viscous fluid in our vibrating-wire device, we decided to conduct a preliminary low pressure measurements on the sample using a capillary viscometer and an Anton Paar vibrating u-tube densimeter for two reasons: 1.) In order to enable us compare our subsequent results that will be obtain using the VWVD device; and, 2.) To enable us identify the most effective solvent and method to be used for cleaning the VWVD device after the measurement is completed. Figures 7.32 and 7.33 show comparisons of the preliminary density and viscosity results obtained using the Anton Paar vibrating u-tube densimeter, the capillary viscometer and that of the VWVD measurements.

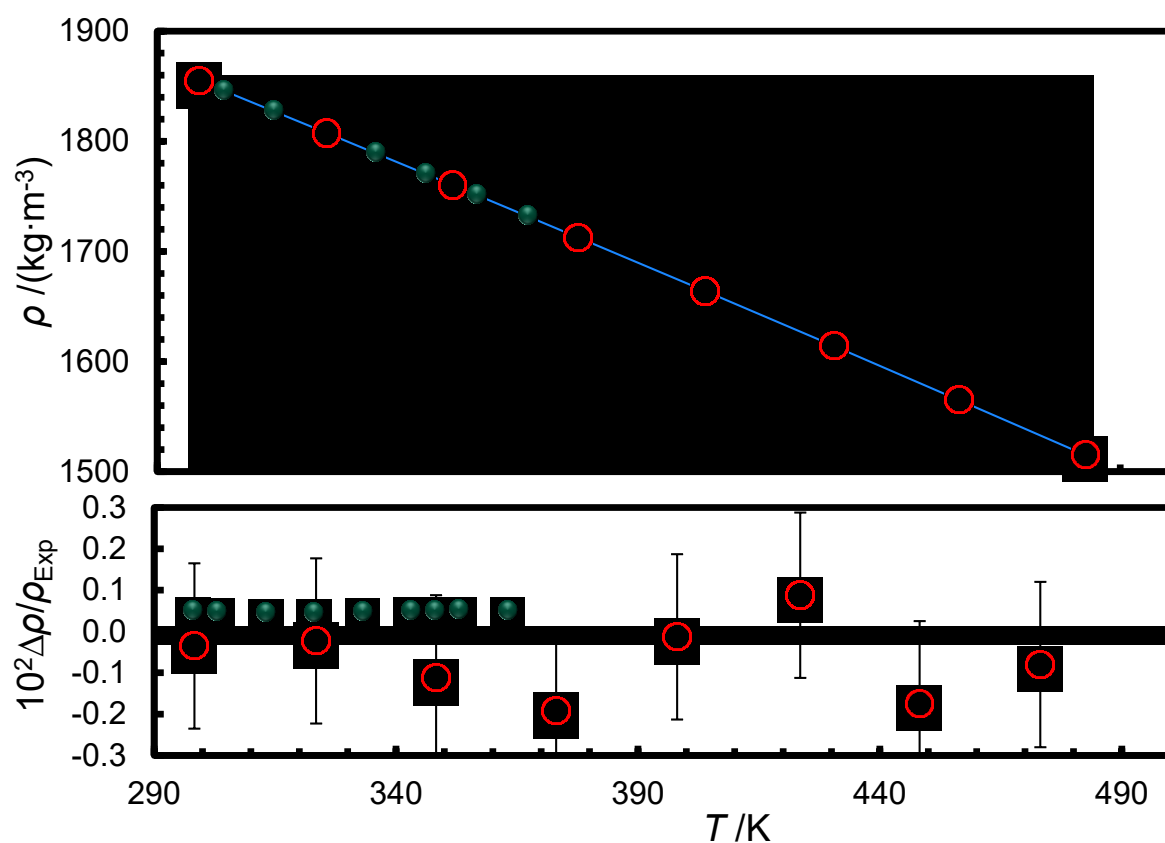


Figure 7.32: Comparison of the density of krytox® at ambient pressure: ●, DMA vibrating tube densimeter data; ○, Vibrating-wire sensor (VWVD) data — eqn. 7.1

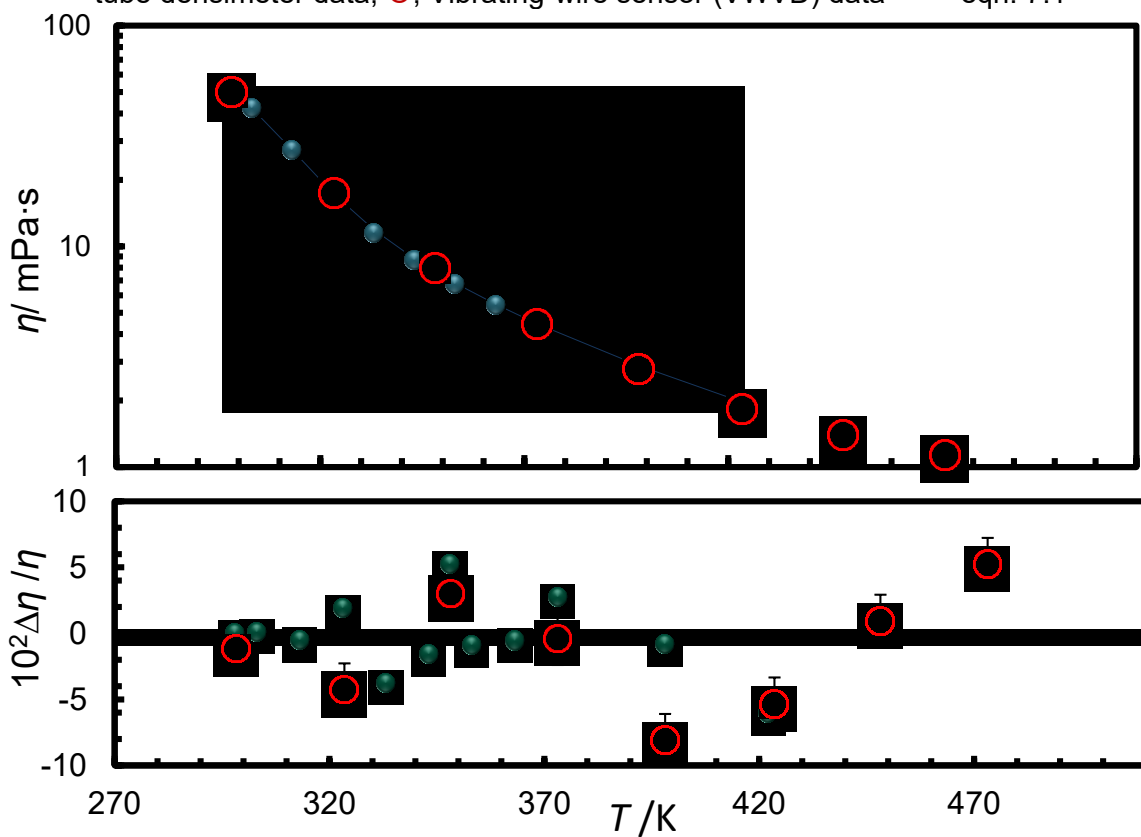


Figure 7.33: Comparison of the viscosity of krytox® at ambient pressure: ●, capillary viscometer along with DMA density data; ○, Vibrating-wire sensor (VWVD) data — eqn. 7.5.

From Figures 7.32 and 7.33 it can be seen that the density measurements from the DMA-5000 Anton Paar vibrating u-tube densimeter and the viscosity data obtained using capillary viscometer are in good agreement with the preliminary ambient pressure results obtained using the VWVD device. The agreement as shown in the deviation plots is typically within 0.2 % for density and 5 % in viscosity. This comparison served as a further validation of our VWVD device for highly viscous and highly dense fluid especially at ambient pressures which gave us the confidence to proceed with the high pressure measurements on krytox® sample.

Although we aimed to measure the viscosity of krytox® across the full working range of temperature (298 to 473) K and pressures (0.1 to 200) MPa of the VWVD device, however, due to the persistent problem of the vibrating-wire and the sinker expanding and touching the bottom of the cell encountered at 473 K, measurements were only possible up to 448 K in the first datasets. Measurement were conducted along each isotherm by increasing pressure from 0.1 MPa up to a corresponding pressure at which the viscosity of the fluid reaches 100 mPa·s. This is to make sure that we are operating within the designed limit for viscosity ($\eta_{\text{Exp.}} \leq 100 \text{ mPa}\cdot\text{s}$) of the VWVD device for which we are confident about the uncertainty of the results. Table B.15 in appendix B presents the results. The properties of the VWVD set up used for these measurements are summarised in Table 7.14 below.

Table 7.14: Properties of vibrating-wires used in this work

Parameter	$x\text{CH}_4 + (1-x)\text{C}_{16}\text{H}_{34}$	$x\text{CH}_4 + (1-x)\text{bC}_{30}\text{H}_{62}$	$x\text{CH}_4 + (1-x)\text{cC}_6\text{H}_{12}$	Krytox®
$R_{w,\text{ave.}} / \text{m}$	7.545167×10^{-5}	7.64999×10^{-5}	7.56100×10^{-5}	7.63517×10^{-5}
$L_{w,\text{ave.}} / \text{m}$	6.612500×10^{-2}	6.5345×10^{-2}	6.43800×10^{-2}	6.49830×10^{-2}
$\rho_w / (\text{kg}\cdot\text{m}^{-3})$	1.92500×10^4	1.92500×10^4	1.92500×10^4	1.92500×10^4
$m_{s,\text{ave.}} / \text{kg}$	4.03625×10^{-1}	4.03625×10^{-1}	4.03509×10^{-1}	4.03566×10^{-1}
$V_{s,\text{ave.}} / \text{m}^3$	1.42382×10^{-4}	1.42382×10^{-4}	1.42382×10^{-4}	1.42434×10^{-4}
$\rho_s / (\text{kg}\cdot\text{m}^{-3})$	2.83335×10^3	2.83335×10^3	2.83335×10^3	2.83335×10^3
f_0 / Hz	8.51464×10^2	8.51464×10^2	8.71362×10^2	8.58436×10^2
Δ_0	6.47024×10^{-5}	3.10000×10^{-5}	2.40280×10^{-5}	2.26212×10^{-5}

The results were correlated for density using the modified Tait equation 7.1 and for viscosity using the Tait-Andrade equation 7.5 by a fitting procedure that minimise in both cases, the absolute average deviations between the experimental data and the corresponding correlating equation. Tables 7.15(a) and (b) present the coefficients of the equations whereas Figures 7.34 and 7.35 illustrate the quality of the correlations.

Table 7.15: Statistical Parameters for the Correlation of Density and Viscosity of Krytox® at Different Compositions and Coefficients of Equations (7.1 to 7.3 and 7.5 to 7.7)

(a) Viscosity			(b) Density		
Coefficient	1 st datasets	2 nd datasets	Coefficient	1 st datasets	2 nd datasets
A_η	9.19×10^{-2}	5.36×10^{-2}	C	8.313×10^{-2}	7.69×10^{-2}
B_η	7.00×10^2	9.23×10^2	a_0	2.687×10^0	2.38×10^0
C_η	1.89×10^2	1.63×10^2	a_1	-3.167×10^{-3}	-1.65×10^{-3}
d_0	-6.03×10^0	1.06×10^1	a_2	1.314×10^{-6}	-3.80×10^{-7}
d_1	2.56×10^1	-2.51×10^1	b_0	2.499×10^2	2.87×10^2
d_2	-1.74×10^1	2.17×10^1	b_1	-9.099×10^{-1}	-1.09×10^0
e_0	-2.71×10^2	3.65×10^2	b_2	8.785×10^{-4}	1.10×10^{-3}
e_1	4.52×10^2	-3.26×10^2	$10^2 \Delta_{AAD,\rho}$	0.241	0.09
e_2	-1.35×10^2	1.09×10^2	$10^2 \Delta_{MAD,\rho}$	0.634	0.19
$10^2 \Delta_{AAD,\eta}$	2.35	1.4	$10^2 \Delta_{bias,\rho}$	-0.012	-0.03
$10^2 \Delta_{MAD,\eta}$	7.40	6.5			
$10^2 \Delta_{bias,\eta}$	0.09	0.04			

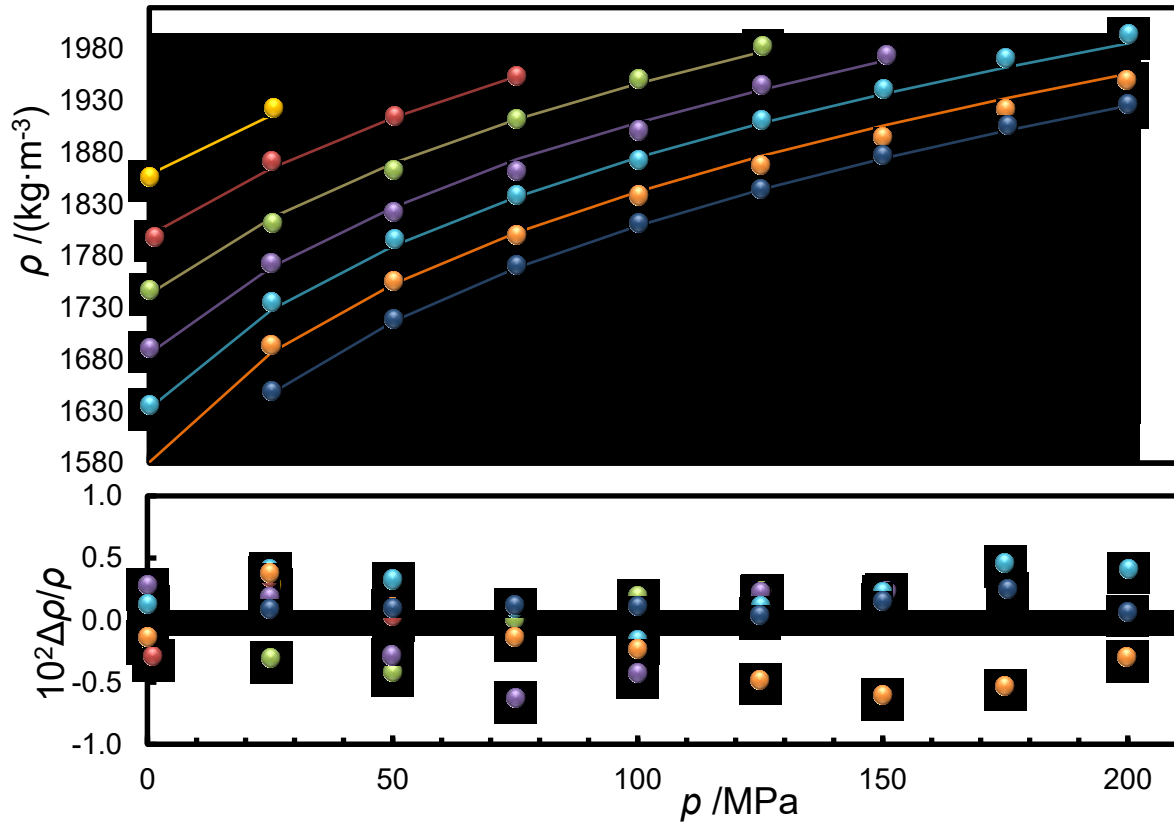


Figure 7.34: Comparison between first experimental density datasets and equation 7.1. ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 348$ K; ●, $T = 373$ K; ●, $T = 398$ K; ●, $T = 423$ K; ●, $T = 448$ K and the lines —, represent the correlating equation 7.1

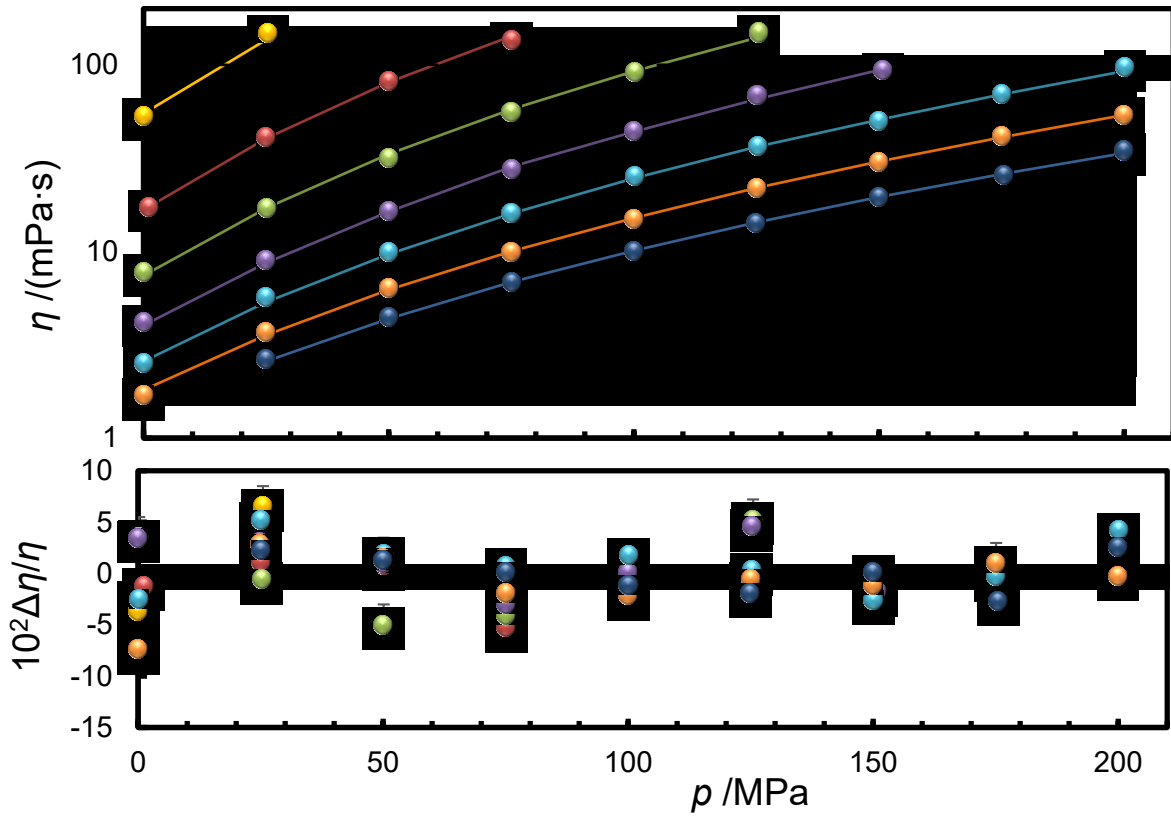


Figure 7.35: Comparison between first experimental viscosity datasets and equation 7.7.
 ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 348$ K; ●, $T = 373$ K; ●, $T = 398$ K; ●, $T = 423$ K; ●, $T = 448$ K and the lines —, represent the correlating equation 7.5

From Figure 7.34 it can be seen that the correlating equation 7.1 described the experimental density data with maximum absolute deviation $\Delta_{\text{MAD},\rho}$ of 0.63 %, average absolute deviation and $\Delta_{\text{MAD},\rho}$ of 0.24 %. On the other hand, it was observed from Figure 7.35 that equation 7.5 described the experimental viscosity with $\Delta_{\text{MAD},\eta}$ of 7.4 % and $\Delta_{\text{AAD},\eta}$ of 2.35 %. Although, weak positive biases (0.012 and 0.09) % for both density and viscosity were obtained from the equations, however we note that both correlations poorly reproduce the experimental data as the Δ_{MADs} and Δ_{AADs} observed in both cases are significantly higher than expected from the equations. This, coupled with the initial demand to measure the viscosity of krytox® at 473 K and 200 MPa prompted the decision to repeat the measurements. To be able to measure up to 473 K, the length of the vibrating-wire needed to be adjusted and the vacuum properties (i.e. the logarithmic vacuum decrement and the vacuum resonance frequency) needed to be re-determined accordingly.

Subsequently, the length of the vibrating-wire was adjusted and the repeat measurements were conducted across the full temperature working range (298 to 473) K of the device. Table B.16 in appendix B presents the results and in a similar way as highlighted above, these results were correlated for density using equation 7.1 and for viscosity by means of

equation 7.5. The coefficients of the correlations are shown in Tables 7.15(a) & (b) and, Figures 7.36 & 7.37 present comparison of these correlations against the second experimental data for density and viscosity respectively. Again, Tables 7.14(a) and (b) show the statistical parameters for the viscosity and density correlations respectively.

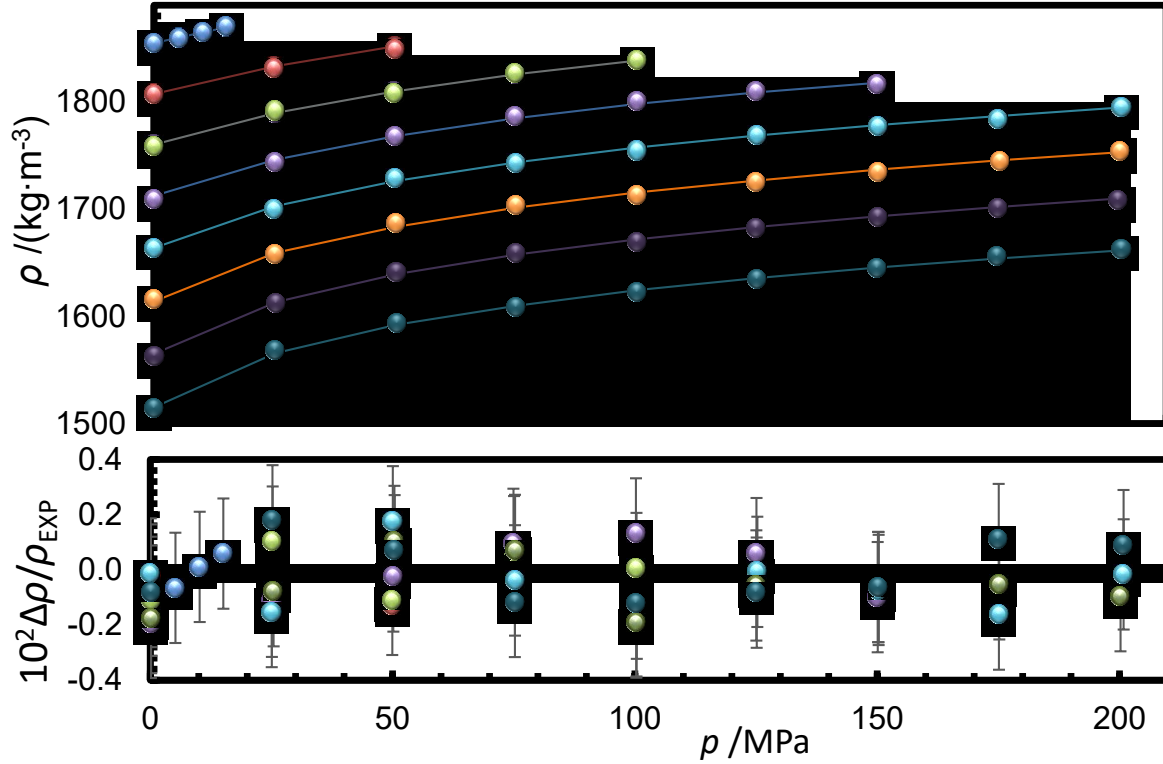


Figure 7.36: Comparison between second experimental density datasets and equation 7.1: ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 348$ K; ●, $T = 373$ K; ●, $T = 398$ K; ●, $T = 423$ K; ●, $T = 448$ K; ●, $T = 473$ K and the lines —, represent the correlating equation 7.1

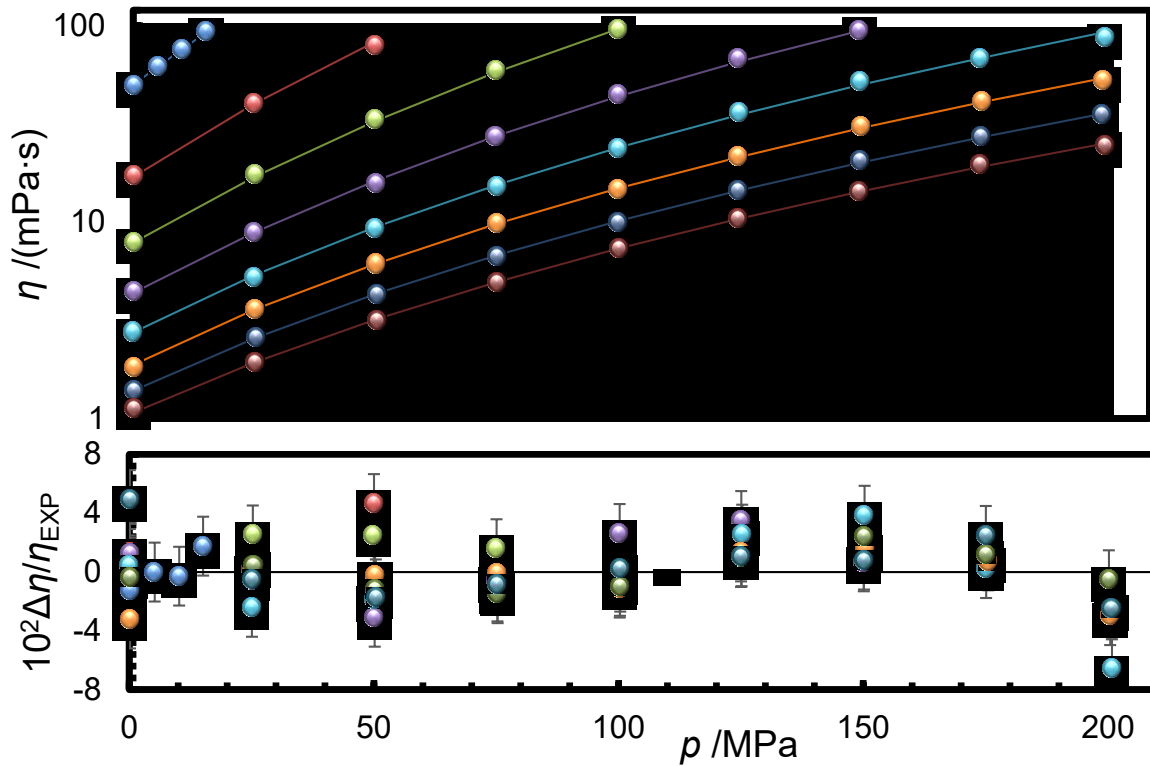


Figure 7.37: Comparison between second experimental viscosity datasets and equation 7.7. ●, $T = 298$ K; ●, $T = 323$ K; ●, $T = 348$ K; ●, $T = 373$ K; ●, $T = 398$ K; ●, $T = 423$ K; ●, $T = 448$ K; ●, $T = 473$ K and the lines —, represent the correlating equation 7.5

It can be seen from Figures 7.36 and 7.37 that both correlating equations 7.1 for density and 7.5 for viscosity described the second datasets better than the first datasets with deviations within ± 0.2 % in density and ± 6.5 % in viscosity.

Although, good internal consistencies were observed in both datasets, however, looking critically at Tables 7.15(a) and (b), it can be seen that the coefficients of both equations 7.1 and 7.5 differ significantly for the two datasets. These differences are illustrated in Figures 7.38 and 7.39 by comparing the experimental results of the two datasets and the respective correlating equations 7.1 for density and 7.5 for viscosity using coefficients obtained by fitting the second datasets as shown in Tables 7.15 (a) and (b).

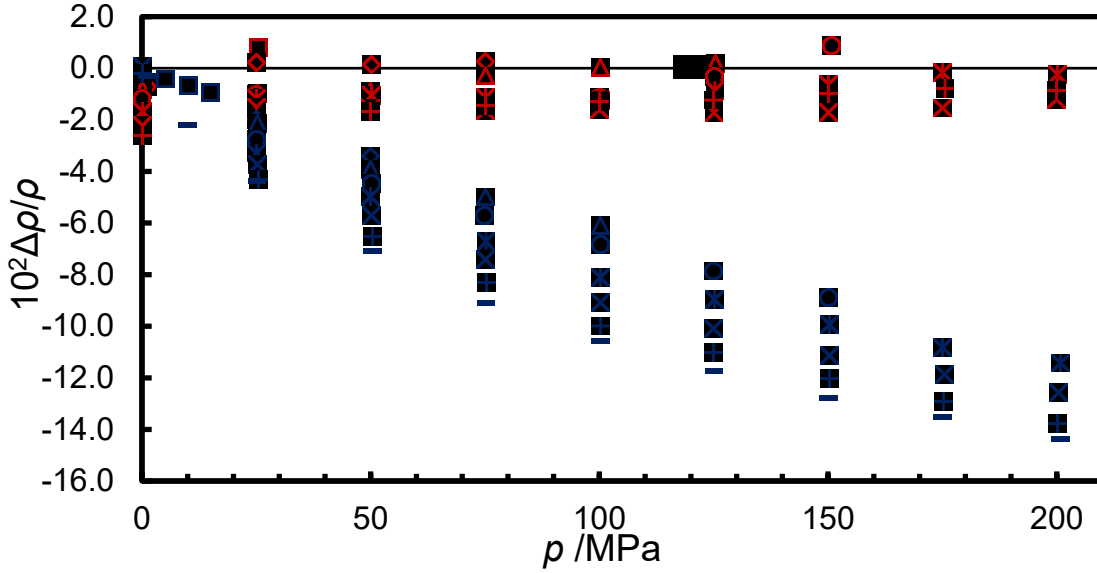


Figure 7.38 Fractional deviations of experimental density from equation 7.1 for the two datasets. Red symbols denote the first datasets and blue symbols represent the second datasets. $\square$, at $T = 298$ K; $\diamond$, at $T = 323$ K; $\triangle$, at $T = 348$ K; $\circ$, at $T = 373$ K; $*$, at $T = 398$ K; $\times$, at $T = 423$ K; $+$, at $T = 448$ K and $-$, at $T = 473$ K

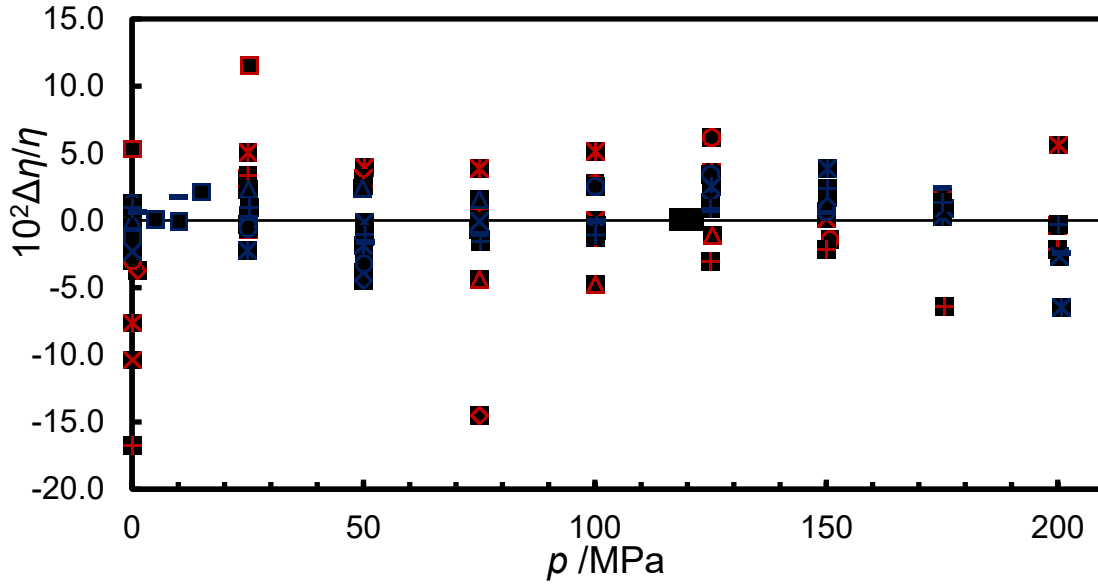


Figure 7.39 Fractional deviations of experimental viscosity from equation 7.5 for the two datasets. Red symbols denote the first datasets and blue symbols represent the second datasets. $\square$, at $T = 298$ K; $\diamond$, at $T = 323$ K; $\triangle$, at $T = 348$ K; $\circ$, at $T = 373$ K; $*$, at $T = 398$ K; $\times$, at $T = 423$ K; $+$, at $T = 448$ K and $-$, at $T = 473$ K

As can be seen from Figure 7.38, the second datasets deviated from the first datasets with maximum deviation $\Delta_{\text{MAD},\rho}$ of about 14.4 % in density. It was also observed that the deviations increases as the pressure increases. For viscosity however, the first datasets

deviated $\Delta_{MAD,\eta}$ from the second datasets with a maximum deviations of about 16.8 % with no any trend in either temperature or pressure was observed.

7.8.1 Comparison with Literature

In order to ascertain the quality of the results, both datasets were compared with published correlations for the same lot of the sample available in the literature. For density, Tait correlation based on measurements on the same lot of the sample produced recently by Comuñas *et al.*[55] in the temperature range (278.15 to 398.15) K and pressure up to 120 MPa was employed. As reported in the paper, this correlation described their experimental data with maximum deviation $\Delta_{MAD,\rho}$ of 0.05 % and $\Delta_{AAD,\rho}$ of 0.01 %. Table 7.16 presents the deviations our datasets obtained in this work and well as those from the correlation in this work and some other available literature.

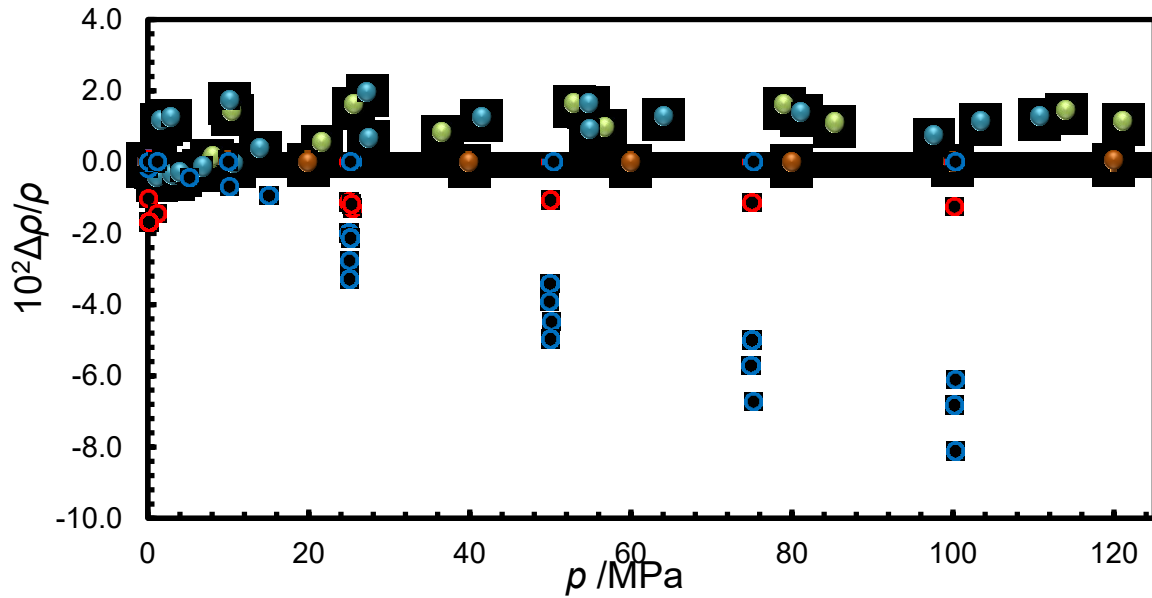


Figure 7.40. Deviations of experimental density from Tait correlation of Comuñas *et al.*[68].
 ●, Comuñas *et al.* (HPM)[55]; ●, Comuñas *et al.* (Stabinger)[55]; ○, This Work dataset 1; ○, This Work dataset 2; ●, Haris[56]; ●, Bamgbade *et al.*[50]; and ● Baled *et al.*[57, 58]

From Figure 7.40, it was evident that both datasets from this work deviated from the reference Tait correlation of Comuñas *et al.*[55]. Furthermore, it can be seen from the that that the first dataset deviated from the correlation with an $\Delta_{MAD,\rho}$ of about 1.69 %, on the other hand, the second dataset, deviated with $\Delta_{MAD,\rho}$ up to 8 %. Moreover, it was observed that the deviations from the second dataset systematically increase with increase in pressure. Comparisons with some other literature density datasets were also made in the table. As can be seen, data from Harris.[56], Bamgbade *et al.*[50] and Baled *et al.*[57, 58] deviated from the correlation with $\Delta_{MAD,\rho}$ of 0.03 %, 1.97 % and 1.66 %

respectively. It is however important to note that Baled *et al.*[57, 58] measured the density of a different lot (K1537) of the sample whereas, in the case of Bamgbade *et al.*[50]'s data, no indication of the lot number was made. Harris[56] measured the density of the same lot (K2391), however, data were only gathered at atmospheric pressure in the temperature range (273.15 to 363.15) K.

In a similar manner, the viscosity obtained from both first and second measurements were compared with a recently developed correlation based on the viscosity data of the same lot of the sample measured in the temperature range (282 to 364) and pressure up to 20 MPa by Mylona *et al.*[59]. The correlation was based on the extended hard sphere scheme of Ciotta *et al.*[60] and it was obtained by optimising the characteristic core volume V_0 and the roughness factor R_η terms in the model against the experimental data. An optimum value of $R_\eta = 3.3 \pm 0.005^{2311}$ was reported, and the characteristic core volume was expressed as function of temperature according to the following equation:

$$V_0 / (\text{m}^3 \cdot \text{mol}^{-1}) = 9.60837610 \times 10^{-4} - 7.461234 \times 10^{-7} (T/\text{K}) + 6.016604 \times 10^{-10} (T/\text{K})^2 \quad (7.8)$$

This correlation described their data with $\Delta_{\text{MAD},\eta}$ of 2.5 % (at 95 % confidence level) and was used to compare our two datasets and other available data in the literature. Table 7.17 shows deviations of our data from this correlation while, Table 4.1 (in section 4) presents the coefficients of the universal curve used in this fitting.

Table 0.16: Deviations of experimental viscosity data from Mylona *et al.*[72]'s correlation

Source	$10^2 \Delta_{\text{AAD},\eta}$	$10^2 \Delta_{\text{bias},\eta}$	$10^2 \Delta_{\text{MAD},\eta}$
Mylona <i>et al.</i> [59] (vibrating-wire)	0.7	-0.0	1.9
Mylona <i>et al.</i> [59] (Coaxial cylinders)	1.2	-1.0	3.0
This Work dataset 1	3.6	3.6	5.7
This Work dataset 2	8.9	13.8	30.3
Harris[56]	1.8	-0.6	5.7
Bair[61] (Alpha viscometer)	2.3	2.3	3.9
Baled[57, 58]	8.4	8.4	9.0
Baled <i>et al.</i> [62]	4.6	4.6	4.8

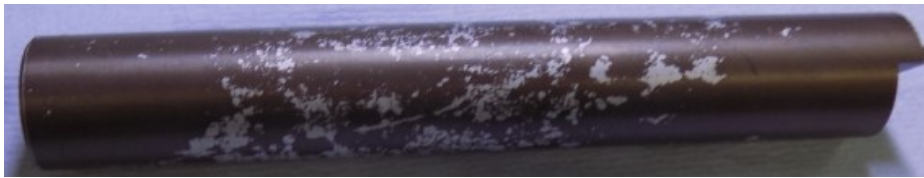
From Table 7.16, while the first dataset produced relatively smaller deviations ($\Delta_{\text{MAD},\eta} = 5.7$ %), significantly large deviations up to 30 % were observed from the second datasets against the reference correlation from Mylona *et al.*[59] In the case of the first datasets, only three data points are within the temperature and pressure ranges for which the correlation was developed. In comparison with other available literature data, the correlation (within the range of its validity) was able to reproduce the data for the same lot (K2391) reported by Harris[56], Baled *et al.*[62] and Bair[61] with $\Delta_{\text{MAD},\eta}$ better than 5 %

and, 9.0 % for the different lot (K1537) data reported by Baled *et al.*[57, 58]. Again, as mentioned earlier that it is not surprising that the deviations from the Baled *et al.*[57, 58] were slightly larger than those from the same lot as it is well known that viscosity of krytox® could differ from one lot to the other. It is also important to state that these comparisons were applied in the temperature and pressure ranges covered by the authors of the two correlations as reported in Comuñas *et al.*[55] for density and Mylona *et al.*[59] for viscosity.

In summary, from the above comparisons, it was observed that both datasets from the present work deviated from the published correlations and other literature data. While the first dataset is comparable to some of the literature data, the second dataset deviated significantly both in terms of density and viscosity. These deviations could be partly attributed to some compatibility issues between the anodised aluminium sinker and krytox® oil and/or the Vertrel™ FX (the recommended solvent used for cleaning the VWVD device after measuring krytox®). This claim followed as a results of visual observations of the aluminium sinker after completing the second measurements and the apparatus was cleaned using the aforementioned solvent (i.e. Vertrel™ FX), in which we observed that some parts of the anodisation around the aluminium sinker surface have been washed-away as shown in Figure 7.39(b). This could further lead to possible contamination of the krytox® oil being measured within the system. It is also possible that the material of anodisation washed-away from the sinker got deposited around the surface of the vibrating wire, which is also detrimental to the accuracy of the experiment as it could lead to the possible corrosion of the wire and ultimately, alter the roughness as well as the size (i.e. radius) of the wire. Moreover, the wire could also act as a catalyst for some decomposition of the fluid depending on the composition and/or nature of the foreign material deposited on it. Efforts to further investigate these problems were hampered by shortage of time and also lack of used-krytox® sample, as the waste bottles containing the left-over of the krytox® have been disposed-off after the measurements for safety and housekeeping purposes. Figure 7.41 show pictures of the anodised aluminium sinker before and after the krytox® measurements.



(a)



(b)

Figure 7.41: Pictures of the anodised aluminium sinker (a) before and (b) after the krytox[®] measurements

Although there were some changes in the properties (i.e. mass and volume) of the sinker before and after the measurements on krytox[®], however, such changes cannot fully explain or justify the differences between the results of our two datasets and/or the literature sources. Nevertheless due to the fact that our measurements were made in absolute mode which means the accuracy of the results depends largely on the accuracy with which these parameters (including mass and volume of the sinker as well as the radius of the wire) were determined, this would significantly influence the accuracy of our results. On this basis, we note that our measurements of the density and viscosity of krytox[®] in both datasets are in error and therefore should be used with caution.

7.9 Viscosity modelling

Although, it is extremely difficult to model the viscosity of highly asymmetric mixtures such as a mixture methane + hexadecane, or methane + squalane, however, in line with the broad objectives of this work, the results obtained were used to attempt to analyse the viscosity of these type mixtures. As mentioned in the introductory part of this thesis, two theoretical models have been identified for this purpose namely: the Vesovic-Wakekham model and the hard sphere model of Dymond-Assael. However, it was later discovered that the original hard sphere model of Dymond Assael is not suitable for some of the mixtures investigated in this study and the reasons for this were highlighted in section 1.3. Nevertheless, the extended hard sphere model described in section 4.4 was employed in the analysis.

7.8.2 The extended hard sphere model

Following the same procedure as described by Dymond and Assael in the original hard sphere model, Ciotta[3], expressed the characteristic core-volume V_0 of many pure substances including hexadecane and methane as quadratic function of temperature by fitting large experimental viscosity datasets in the range of (298 to 400) K. For instance, for pure hexadecane, experimental viscosity data from [3, 6, 9, 46] were used in fit and the coefficients of the fit are reported in [3].

$$V_0 = \sum_{i=0}^3 g_i (T/K)^i, \quad (7.9)$$

It is important to note that the V_0 correlation for pure hexadecane, methane and hexadecane were extended to cover temperature range up to 473.15 K as part of this work by following similar approach described by Ciotta[3], and hence the cubic temperature dependence of V_0 shown in equation 7.9. The coefficients of equation 7.10 are shown in Table 4.1 in section 4, whereas those of equation 7.9 are presented in Table 7.20.

The correlations for roughness factor and core volume as given in the original hard sphere model were used. For instance, to compute the R_η for the pure methane the following equation was used.

$$R_\eta = 0.995 - 0.0008944 C_n + 0.005427 C_n^2 \quad (7.10)$$

For squalane and cyclohexane, coefficients of both the roughness factor and the characteristic core volumes of the pure species were obtained by fitting available experimental data in a similar approach used by Ciotta *et al.*[63, 64] to obtain these data for the pure hexadecane as described above.

To apply this model to binary mixtures, the properties of the mixtures were estimated from those of the individual components via a mixing rule. Usually, a simple linear mole fraction average is employed for simple mixtures of similar molecules. However, for highly asymmetric mixtures the linear mixing rule usually do not give satisfactory estimation of the mixture viscosity. In this work several mixing rules given in the following sections have been tested to predict the viscosities of the different binary mixtures investigated.

A. Linear mixing rule:

To start with, two linear mixing rules that express the characteristic core volume of the mixture as a function of core volumes of the individual components and their mole fractions were tested.

i. A conventional linear mole fraction averages of V_0

The conventional linear mixing rule described the characteristic core volume and the roughness factor $R_{\eta,\text{mix}}$ of the mixture $V_{0,\text{mix}}$ as a mole-fraction-averages of the respective core volumes $V_{0,i}$ and the roughness factors $R_{\eta,i}$ of the individual components in the mixture, and for a binary mixture, the two properties are given by:

$$V_{0,\text{mix.}} = \sum_{i=1}^2 x_i V_{0,i}, \quad R_{\eta,\text{mix.}} = \sum_{i=1}^2 x_i R_{\eta,i}, \quad (7.11)$$

where, $V_{0, \text{mix}}$ is the characteristic core volume of the mixture, and $V_{0,i}$ & $V_{0,j}$ are the respective core volumes of the pure components i and j .

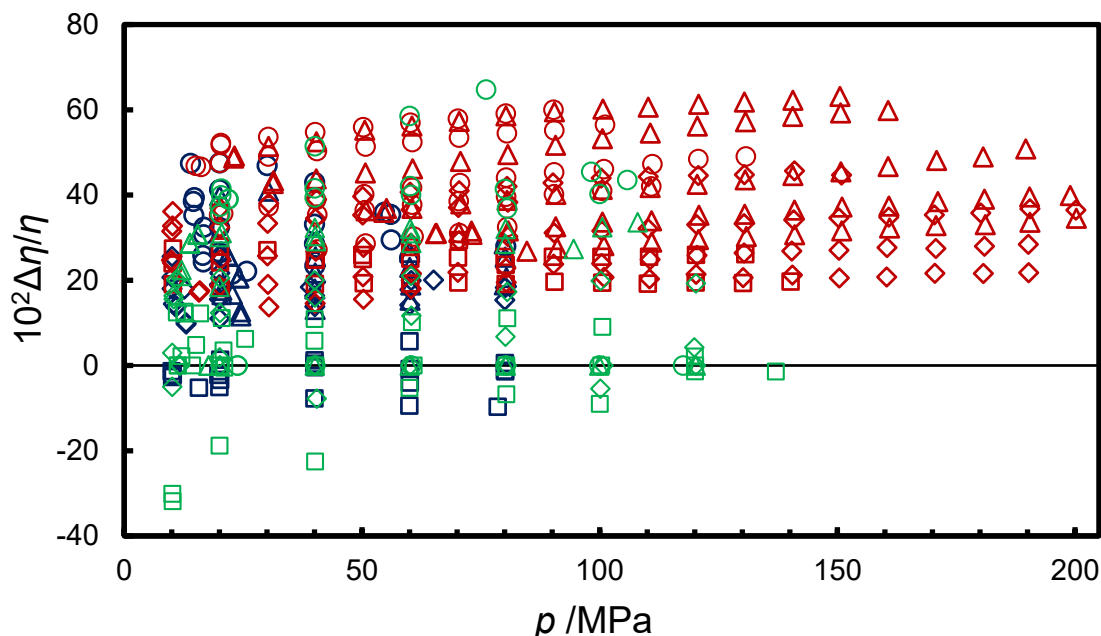


Figure 7.42 Relative deviations of equations 7.9 along with 7.13 from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{C}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{C}_{30}\text{H}_{62}$

Figure 7.42 shows a combined deviation plot for the three binary systems for this scheme. It can be seen from the figure that the deviations from the experimental data for all the three binary systems at methane compositions $x = (0.1 \text{ to } 0.4)$ are up to 65 % with the highest deviation observed from the mixture of methane + squalane at $x = 0.4052$. It was also observed that the deviations increase systematically with increase in pressure and mole fractions of methane for all the three systems.

Figure 7.43 shows the plot of maximum absolute deviations $\Delta_{\text{MAD},\eta}$ against mole fraction of methane x for the three systems. From the figure it was observed that the maximum absolute deviations $\Delta_{\text{MAD},\eta}$ for both binary systems of methane + hexadecane and methane + cyclohexane increase systematically as the mole fraction x of methane increases. Similar trend was observed for the methane + squalane system except that there is slight decrease in the $\Delta_{\text{MAD},\eta}$ at methane mole fraction $x = 0.2$.

Overall, it was observed that the $\Delta_{\text{MAD},\eta}$ of both mixtures of methane + cyclohexane and that of methane + squalane were bigger than those of the methane + hexadecane at methane mole fractions of $x = 0.1$ and $x = 0.4$ and the trend is as follows:

$$\Delta_{\text{MAD},\eta} \text{ C1+bC30} > \Delta_{\text{MAD},\eta} \text{ C1+cC6} > \Delta_{\text{MAD},\eta} \text{ C1+C16}$$

This is not surprising considering the fact that both squalane and cyclohexane have more complex chemical structures, in that, the former belongs to a branched aliphatic hydrocarbon family and the latter belongs to the cyclo-group of the aliphatic hydrocarbon and hence, the degree of asymmetry of their mixtures with methane is more than that of methane + hexadecane which is a straight chain hydrocarbon.

For the methane mole fractions of $x = 0.2$ and $x = 0.3$, a particular trend was observed in which the $\Delta_{MAD,\eta}$ for the methane + cyclohexane is larger than that of methane + hexadecane and methane + squalane and this trend is as shown below:

$$\Delta_{MAD,\eta} \text{ C1+C6} > \Delta_{MAD,\eta} \text{ C1+C16} > \Delta_{MAD,\eta} \text{ C1+bC30}$$

It is important to note that this mixing rule was applied without any adjustable parameter, and therefore it is not surprising that it produced large deviations due to the highly asymmetric nature of the mixtures concerned as similar deviations were observed by Ciotta *et al.*[24] in the case of CO_2 + squalane mixtures.

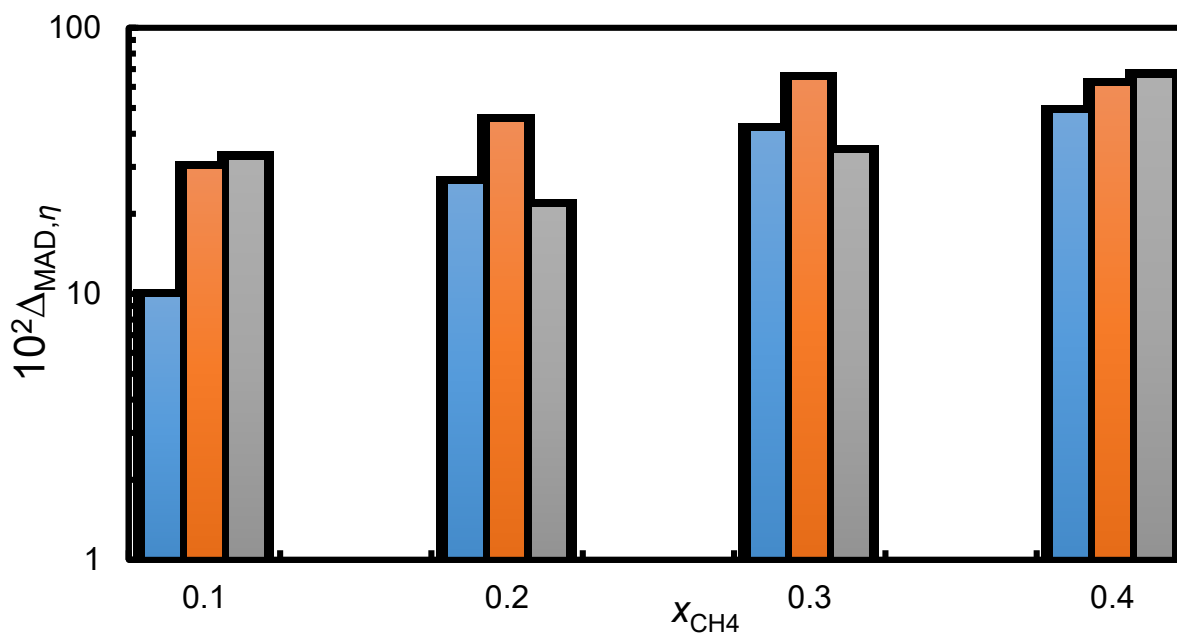


Figure 7.43: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of equations 7.19 and 7.13 from the experimental viscosity data for the three binary systems: A. ■, blue bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; B. ■, orange bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; and C. ■, grey bars represent $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$.

In an attempt to improve the viscosity prediction, several approaches (both predictive and correlative) were tested in the estimation of the characteristic core volume of the mixtures $V_{0,\text{mix}}$ and subsequently applied to the extended hard sphere model. In the following sections, some of these approaches were highlighted.

ii. Linear mixing rule with an additional index parameter γ

Here, while maintaining the same linear form of equation 7.11, additional parameter γ was introduced as an index to both sides of the $V_{0, \text{mix}}$ equation as shown in the equation below:

$$V_{0, \text{mix}}^{\gamma} = \sum_{i=1}^2 x_i V_{0,i}^{\gamma} . \quad (7.12)$$

At first, the index parameter γ was set to constant values 1/3 and then later to 2/3, just to maintain the predictive form of the equation. However, as shown in Figure 7.44, the deviations became worse than that observed in the conventional mixing rule for all the three systems in both cases.

Subsequently, the index parameter γ was treated as an adjustable parameter in two scenarios: firstly by letting it to be a single floating fitting parameter; and secondly, an adjustable parameter with linear dependence on temperature as shown in the following equation.

$$\gamma_{\text{ave.}} = \sum_{i=0}^1 r_i (T/K)^i . \quad (7.13)$$

In both cases, the value of fitting parameter(s) is/are obtained from a non-linear fitting procedure that minimise the absolute average deviations of the estimated values from the experimental observations. Again, Figure 7.44 shows the plots of maximum absolute deviations $\Delta_{\text{MAD}, \eta}$ obtained for the three binary systems and Table 7.17 present the coefficients and the average value of the fitting parameter $\gamma_{\text{ave.}}$. It is important to note that in both cases, the fitting procedure was applied to the whole compositions of a given binary system.

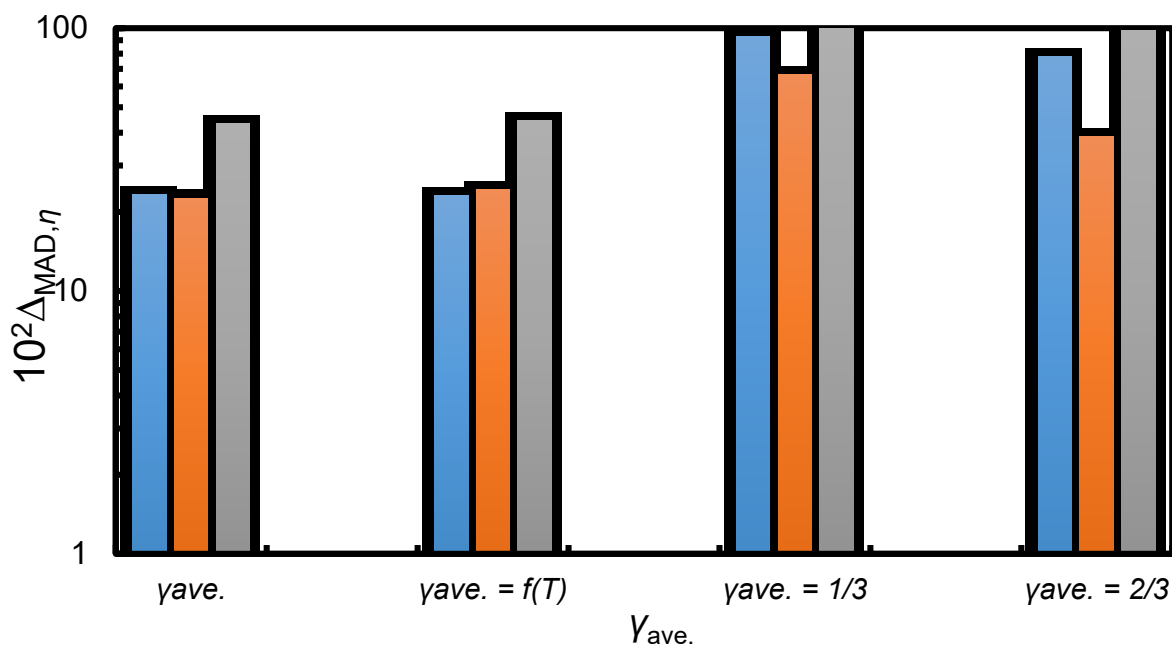


Figure 7.44: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of equations 7.9 along with equations 7.14, or (7.14 and 7.15) from the experimental viscosity data for the three binary systems: A. ■, blue bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; B. ■, orange bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; and C. ■, grey bars represent $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$.

From Figure 7.44, it can be seen that by treating the index, γ as an adjustable parameter, the $\Delta_{MAD,\eta}$ s were reduced by about half of their corresponding values obtained in the previous scheme in all the three systems. However, it was also observed that by making the index parameter a linear function of temperature (thereby increasing the number of fitting parameters to 2) does not produce any significant improvement in all the three binary systems. Therefore, the first scenario in which γ was treated as a single fitting parameter was preferred, and Figure 7.45 shows a combined deviation plots for this scheme for the values of γ for all the three binary systems shown in Table 7.17

Table 0.17: Coefficients of equations 7.12, 7.13, 7.15 and 7.16

system	$\gamma_{ave.}$	r_0	r_1	l_{ij}	s_0	s_1
$\text{CH}_4 + \text{C}_{16}\text{H}_{34}$	9.65E-01	2.74E+02	1.13E-04	2.80E-02	5.79E-02	-9.10E-05
$\text{CH}_4 + \text{cC}_6\text{H}_{12}$	9.25E-01	2.74E+02	-3.35E-04	2.97E-02	5.79E-02	-9.10E-05
$\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$	9.79E-01	2.74E+02	5.16E-04	2.04E-02	2.38E-01	-6.48E-04

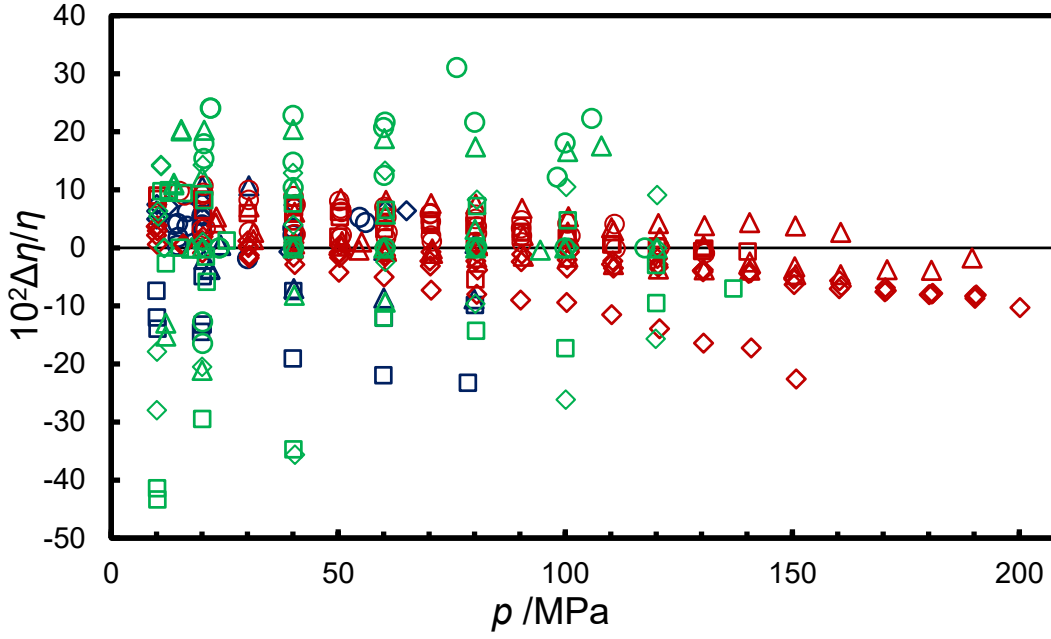


Figure 7.45: Relative deviations of equations 7.11 together with 7.16 from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{cC}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$

Overall, this scheme like the conventional mole-fraction average mixing rule is linear in nature and is relatively simple that incorporated only one adjustable parameter and was able to reduce the maximum absolute deviations $\Delta_{\text{MAD},\eta}$ from 65 % to less than 44 % for all the three binary systems. However, with the introduction of an adjustable parameter, the scheme has become a correlative rather than a predictive approach.

B. A quadratic mixing

Having attempted two forms of linear mixing rules as discussed in the previous sections and considering the small improvement observed when a fitting parameter was added, we consider a quadratic mixing rule of the form shown in the following sections.

i. Simple quadratic mixing rule in mole fraction of the components

$$V_{0,\text{mix.}} = x_i^2 V_{0,ii} + 2x_i x_j V_{0,ij} + x_j^2 V_{0,jj} . \quad (7.14)$$

Here the terms $V_{0,ii}$ and $V_{0,jj}$ are the characteristic core volumes of the components i and j , in the mixture which are identical to the core volumes of the pure species $V_{0,i}$ and $V_{0,j}$. $V_{0,ij}$ is the unlike interaction between the individual components in the mixture and we expressed it as a simple arithmetic mean of the core volumes of the pure species $V_{0,i}$ and $V_{0,j}$ as follows;

$$V_{0,ij} = (1 - I_{ij}) \left(\frac{V_{0,i} + V_{0,j}}{2} \right), \quad (7.15)$$

where, l_{ij} is a binary interaction parameter between i and j pair, and it is treated as an adjustable parameter.

Here, we implemented the scheme in three different scenarios with respect to the interaction parameter l_{ij} in equation 7.15. Firstly, in the predictive form, in which we set the interaction parameter l_{ij} to zero, secondly, by fitting an average value of the interaction parameter l_{ij} , and finally, by making the interaction parameter l_{ij} a linear function of temperature as shown in the equation below.

$$l_{ij} = \sum_{i=0}^1 s_i (T/K)^i. \quad (7.16)$$

We then compare the maximum absolute deviations $\Delta_{MAD,\eta}$ from all these scenarios and select the one with the lowest $\Delta_{MAD,\eta}$ for all the three binary systems. Figure 7.46 presents a comparison of the $\Delta_{MAD,\eta}$ obtained from these scenarios and Table 7.18 presents the coefficients of equations 7.15 and 7.16.

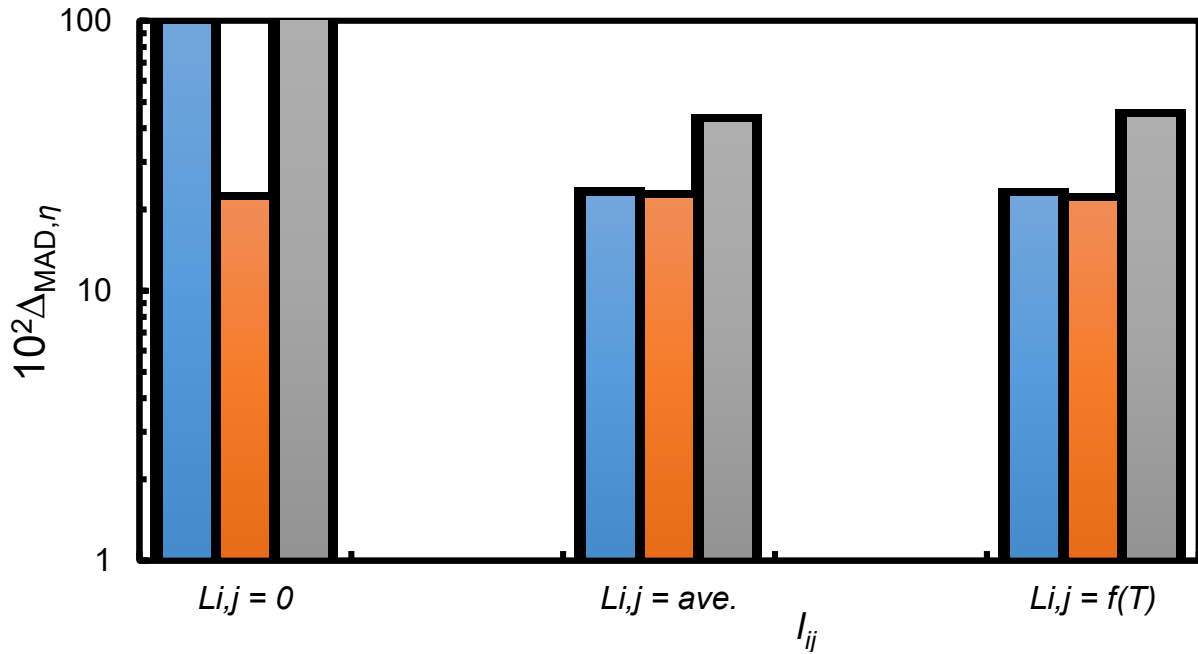


Figure 7.46: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of equations 7.9 along with equations (7.14 & 7.15) or (7.14, 7.15 & 7.16) from the experimental viscosity data for the three binary systems: A. ■, blue bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; B. ■, orange bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; and C. ■, grey bars represent $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$.

From Figure 7.46, it was observed that the predictive approach (i.e. the situation for which $l_{ij} = 0$), present the highest values of $\Delta_{MAD,\eta}$ for both mixtures of methane with hexadecane or squalane relative to the other two scenarios. For the mixtures of methane with cyclohexane however, the values of the $\Delta_{MAD,\eta}$ were very similar for all the three

approaches. This implies that making the adjustable parameter l_{ij} a linear function of temperature (and hence increasing the number of fitting parameters to two) does not make any significant improvement to the prediction. Figure 7.47 shows the combined relative deviation plots for the scenario in which the adjustable parameter was fitted to average values of l_{ij} shown in Table 7.17 for the three binary systems.

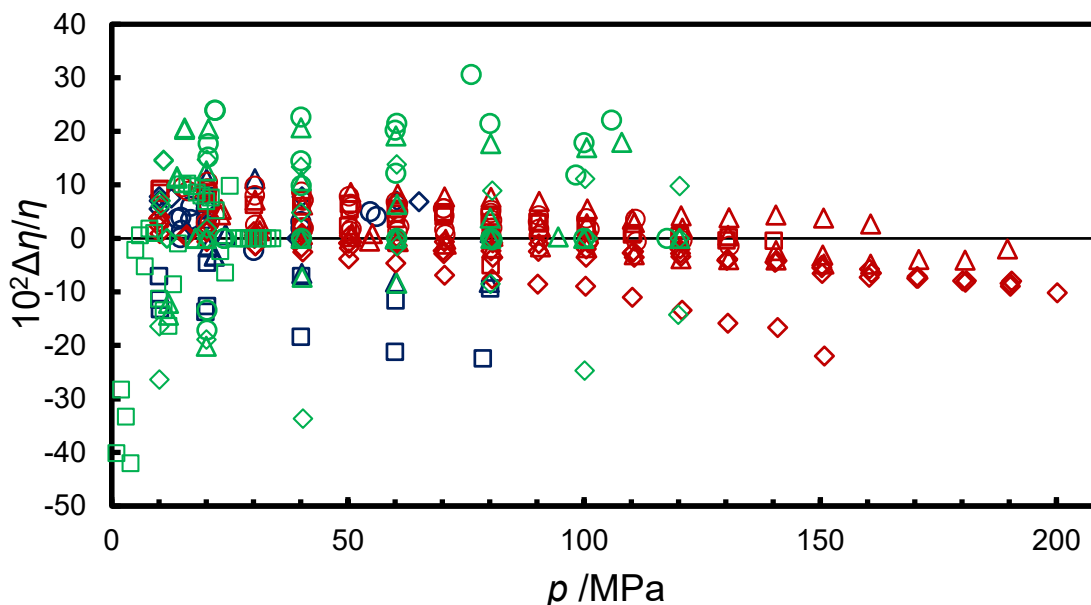


Figure 7.47: Relative deviations of equations 7.9 along with equations (7.14 and 7.15) from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{cC}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$

From 7.47, it can be seen that the relative deviations for the mixtures of methane + cyclohexane were in the range (-22.0 to 10.5) %; while that of methane + hexadecane are distributed in the (-22.4 to 11.1) % and those for the methane + squalane spanned from (-42 to 30.6) %. In all the three systems, it was observed that the relative deviations increase with increasing mole fraction of methane with the exception of methane + hexadecane mixtures at $x = 2976$ for which the deviations were larger than those at $x = 0.3979$.

Generally, the quadratic mixing rule in comparison to the linear mixing rule, slightly improved the predictions as observed in Figures 7.46 and 7.47 for all the three binary systems. In particular, as seen in the binary mixtures of methane + cyclohexane were even the predictive approach of the quadratic mixing rule presented relatively lower $\Delta_{\text{MAD},\eta}$ compared to the corresponding values of $\Delta_{\text{MAD},\eta}$ obtained from both correlative and predictive linear mixing rule approaches discussed above. With respect to the mixtures of methane and hexadecane or squalane, the correlative quadratic mixing rule however,

produced only a marginal improvement in the $\Delta_{\text{MAD},\eta}$ compared to the linear mixing rule with one adjustable parameter γ highlighted in the previous section. Overall, this scheme is relatively more complex mixing rule compared to the previous ones considered, in that, it contains a second degree polynomial in mole fractions of the components and also an adjustable parameters l_{ij} and therefore, it is not surprising that it gave relatively better predictions.

Quadratic in mole fractions and the core volume terms raised to the power of one-third $V_0^{1/3}$

$$V_{0,\text{mix.}}^{1/3} = x_i^2 V_{0,ii}^{1/3} + 2x_i x_j V_{0,ij}^{1/3} + x_j^2 V_{0,jj}^{1/3}. \quad (7.17)$$

Here we applied the same second order expression in mole fraction of the components as shown in equation 7.17, but the characteristic core volume terms in are raised to one-third power, and so was the unlike interaction term $V_{0,ij}^{1/3}$

$$V_{0,ij}^{1/3} = (1 - l'_{ij}) \left(\frac{V_{0,i}^{1/3} + V_{0,j}^{1/3}}{2} \right). \quad (7.18)$$

Again, we implemented this scheme in three different scenarios with respect to the interaction parameter l'_{ij} in equation 7.18: Firstly, in the predictive form, where we set the interaction parameter l'_{ij} to zero; secondly, by fitting an average value of the interaction parameter l_{ij} ; and finally, by making the interaction parameter l'_{ij} a fitting parameter with linear dependence on temperature as shown in the following expression.

$$l'_{ij} = \sum_{i=0}^1 t_i (T/K)^i. \quad (7.19)$$

We then compare the maximum absolute deviations $\Delta_{\text{MAD},\eta}$ from all these scenarios and select the one with the lowest $\Delta_{\text{MAD},\eta}$ for all the three binary systems. Figure 7.48 presents a comparison of the $\Delta_{\text{MAD},\eta}$ obtained from these scenarios and Table 7.18 presents the coefficients of equation 7.18 and 7.19.

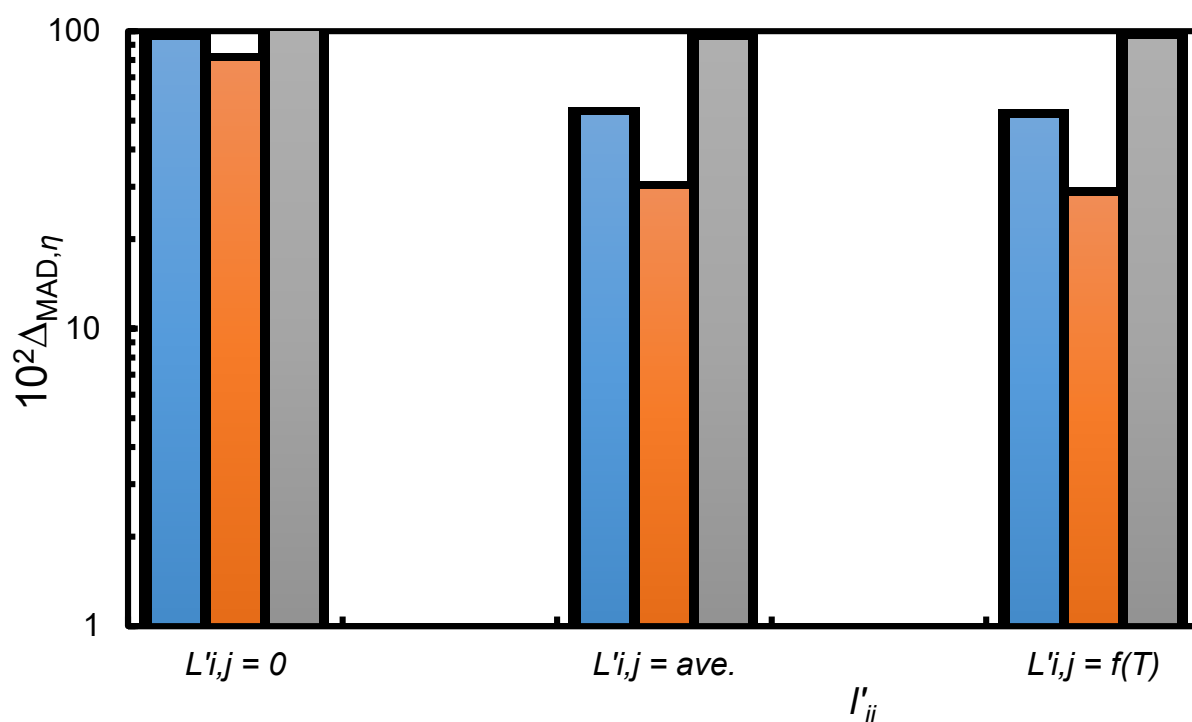


Figure 7.48: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of equations 7.9 along with equations (7.17 & 7.18) or (7.17, 7.18 and 7.19) from the experimental viscosity data for the three binary systems: A. ■, blue bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; B. ■, orange bars represent $\text{CH}_4 + \text{cC}_6\text{H}_{12}$; and C. ■, grey bars represent $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$.

Table 0.18: Coefficients of equations 7.18, 7.19, 7.21 and 7.22

system	t_{ij}	t_0	t_1	l'_{ij}	u_0	u_1
$\text{CH}_4 + \text{C}_{16}\text{H}_{34}$	-2.15E-01	-1.11E-01	-4.86E-05	-1.85E-01	-7.13E-02	-7.80E-05
$\text{CH}_4 + \text{cC}_6\text{H}_{12}$	-8.46E-02	-7.54E-02	-2.83E-05	-7.20E-02	-7.39E-02	5.62E-06
$\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$	-2.83E-01	-1.47E-01	-4.04E-04	-2.44E-01	-8.83E-02	-4.68E-04

It can be seen from Figure 7.48 that the predictive scenario gave the highest values of $10^2 \Delta_{MAD,\eta}$ whereas the two correlative approaches presented nearly the same values of $10^2 \Delta_{MAD,\eta}$ for all the three systems. Again, this implies that making the interaction parameter l'_{ij} a linear function of temperature thereby doubling the number of fitting parameters does not improve the prediction and therefore, it is unnecessary. Figure 7.49 shows the combined relative deviations obtained with the fitted average values of interaction parameters l'_{ij} shown in Table 7.18 for the three binary systems.

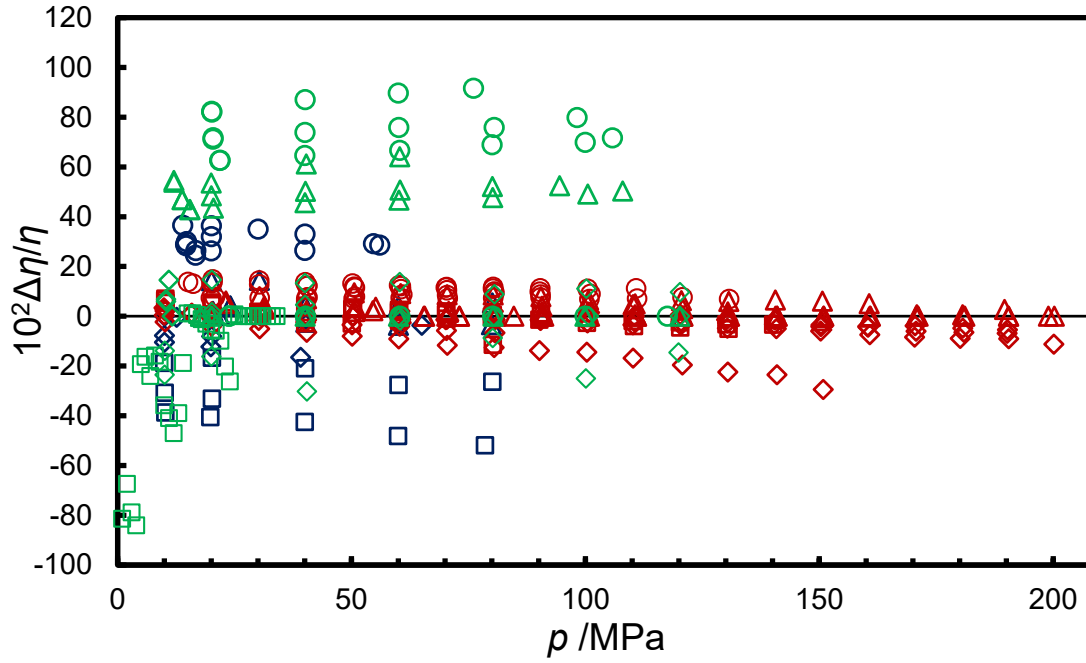


Figure 7.49: Relative deviations of equations 7.9 along with equations (7.19 and 7.20) from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{cC}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$

From Figure 7.49, it can be seen that the deviations from this were scheme sparsely distributed in the range (-84.1 to 91.6) % with the highest deviations being observed in the methane + squalane system. Overall, it is surprising that this mixing rule presented deviations worse than those observed in the previous mixing rules despite the relative complexity of the former.

- ii. Quadratic in mole fractions and core volume terms raised to two-third

$$V_0^{2/3}$$

$$V_{0,\text{mix}}^{2/3} = x_i^2 V_{0,ii}^{2/3} + 2x_i x_j V_{0,ij}^{2/3} + x_j^2 V_{0,jj}^{2/3} \quad (7.20)$$

with the characteristic core-volume interaction between i and j pairs represented as;

$$V_{0,ij}^{2/3} = (1 - I_{ij}'') \left(\frac{V_{0,i}^{2/3} + V_{0,j}^{2/3}}{2} \right) \quad (7.21)$$

I_{ij}'' is the binary interaction parameter

In a similar way, we implemented the scheme in three different scenarios with respect to the interaction parameter I_{ij}'' in equation 7.21: Firstly, in its predictive form, where we set the interaction parameter I_{ij}'' to zero; secondly, by fitting an average value of the

interaction parameter l''_{ij} , and finally, by making the interaction parameter l''_{ij} a linear function of temperature as shown in:

$$l''_{ij} = \sum_{i=0}^1 u_i (T/K)^i \quad (7.22)$$

The coefficients of equations 7.21 and 7.22 shown in Table 7.18 are obtained by a nonlinear regression that minimises the absolute average deviations of the predicted values from the experimental data. Figure 7.50 presents a comparison of the $\Delta_{MAD,\eta}$ obtained from these scenarios.

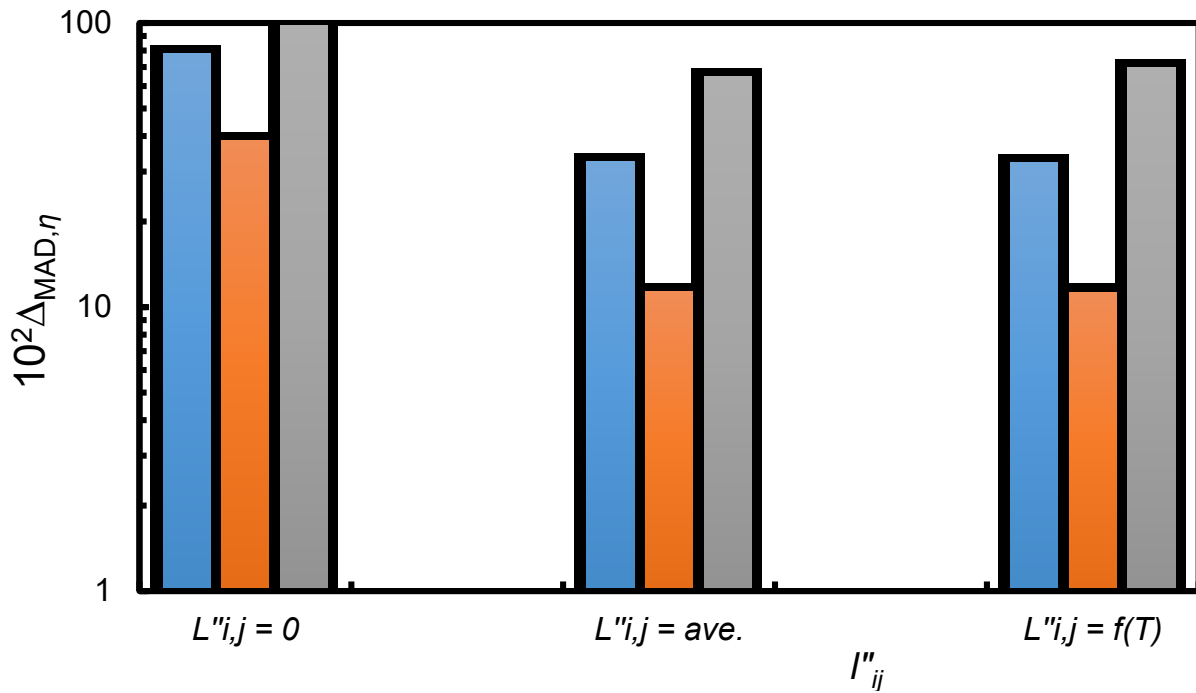


Figure 7.50: Maximum absolute relative deviation $10^2 \Delta_{MAD,\eta}$ of equations 7.9 combined with equations (7.20 & 7.21) or (7.20, 7.21 and 7.22) from the experimental viscosity data for the three binary systems: A. ■, blue bars represent CH₄ + cC₆H₁₂; B. ■, orange bars represent CH₄ + cC₆H₁₂; and C. ■, grey bars represent CH₄ + bC₃₀H₆₂.

It is evident from Figure 7.50 that the predictive approach of this scheme failed to reproduce the experimental data as it presented deviations up to 98 % in the case methane + squalane binary systems. Furthermore, when an adjustable parameter l''_{ij} is introduced, significant reduction in the maximum absolute deviations $\Delta_{MAD,\eta}$ were noticed across all the three binary systems. However, it was observed that doubling the number of fitting parameter by making the adjustable parameter l''_{ij} a function of temperature with linear dependence does not make any noticeable improvement in the prediction and hence not necessary. Figure 7.51 shows a plot of combined deviations of all the three

binary systems obtained by fitting one single temperature-independent adjustable parameter I''_{ij} for each system shown in Table 7.18.

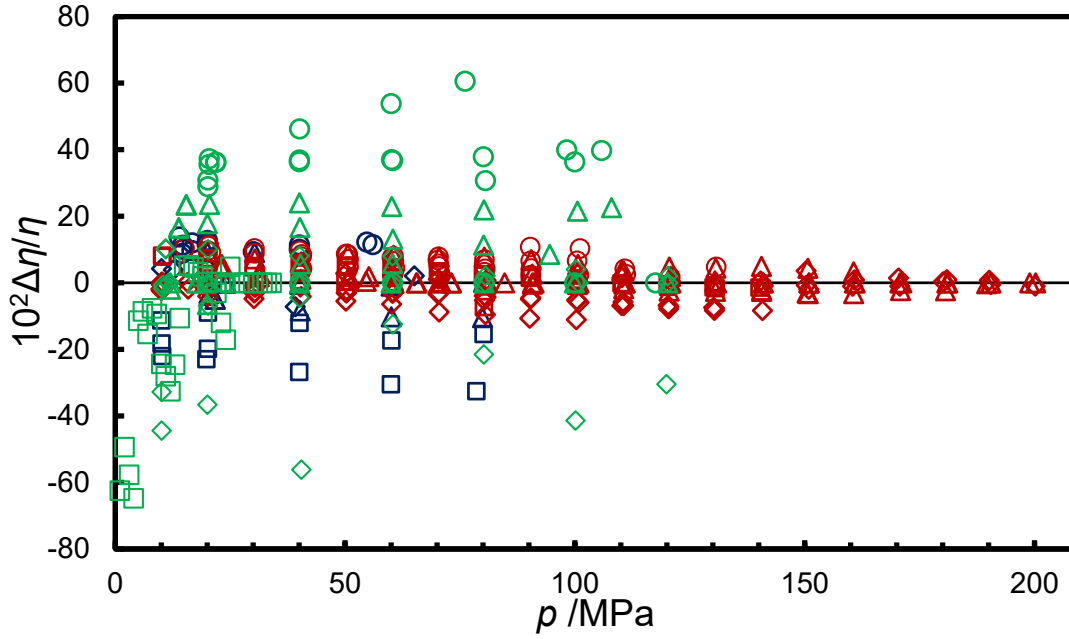


Figure 7.51: Relative deviations of equations 7.9 combined with equations (7.20 and 7.21) from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{cC}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$

From Figure 7.51, it can be seen that the deviations for the three binary systems were distributed in the range $(-11.1 \text{ to } 11.3)\%$, $(-32.6 \text{ to } 13.8)\%$ and $(-64.7 \text{ to } 60.6)\%$ respectively for mixtures of methane + cyclohexane, methane + hexadecane and methane + squalane respectively. Furthermore, as seen in the previous schemes, larger deviations were again observed from the methane + squalane system and, this is not surprising considering the degree of asymmetry of this mixture.

Overall, although this scheme presented better estimation compared to the previous one however, it gave slightly higher deviations especially for the $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$ binary systems and with no any particular trend observed with the mole fraction and/or pressure increase.

C. Treating $V_{0,\text{mix}}$ as an adjustable parameter

In this approach, the characteristic core volume of the mixture $V_{0,\text{mix}}$ for each composition was treated as a fitting parameter and was expressed as a quadratic function of temperature presented in the following equation:

$$V_{0,\text{mix.}} = \sum_{i=0}^2 g_i (T/\text{K})^i. \quad (7.23)$$

The parameters of equation 7.23 shown in Table 7.19 for the three binary systems were optimized for each composition of a given binary system by a non-linear regression. The analysis minimized the sum of the square deviations of the calculated values from the experimental data. Figure 7.52 presents the plots of combined deviations of all the three binary systems for all methane compositions investigated in this work.

Table 0.19: Parameters of the Extended HS Model Equation 7.11 for all three systems

Coefficient	$x_1 = 0.0$	$x_1 = 0.1013$	$x_1 = 0.2021$	$x_1 = 0.2976$	$x_1 = 0.3976$
R_η	1.820×10^0	1.737×10^0	1.654×10^0	1.576×10^0	1.494×10^0
g_0	2.763×10^2	3.002×10^2	2.627×10^2	3.159×10^2	1.767×10^2
g_1	-2.395×10^{-1}	-5.309×10^{-1}	-4.312×10^{-1}	-8.606×10^{-1}	-1.753×10^{-1}
g_2	1.669×10^{-4}	6.328×10^{-4}	5.104×10^{-4}	1.134×10^{-3}	1.589×10^{-4}
g_3	-1.900×10^{-9}	-1.004×10^{-8}	0.000×10^0	0.000×10^0	0.000×10^0
$10^2 \Delta_{AAD}$	2.45	1.36	1.55	1.05	1.31
$10^2 \Delta_{MAD}$	5.16	3.03	3.96	3.15	3.38
$10^2 \Delta_{bias}$	2.10	0.15	0.16	0.10	0.07
$CH_4 + cC_6H_{12}$					
Coefficient	$x_1 = 0.0992$	$x_1 = 0.2073$	$x_1 = 0.3031$	$x_1 = 0.4020$	$x_1 = 1$
R_η	9.636×10^{-1}	9.679×10^{-1}	9.718×10^{-1}	9.757×10^{-1}	9.995×10^{-1}
g_0	8.347×10^1	7.042×10^1	6.592×10^1	5.796×10^1	1.038×10^2
g_1	-5.593×10^{-2}	-2.332×10^2	-2.599×10^{-2}	-1.501×10^{-2}	-1.178×10^0
g_2	4.921×10^{-5}	5.999×10^{-6}	5.909×10^{-6}	-5.389×10^{-6}	4.987×10^{-3}
$10^2 \Delta_{AAD}$	3.15	2.29	2.53	3.28	0.27
$10^2 \Delta_{MAD}$	9.22	6.80	6.77	7.12	1.18
$10^2 \Delta_{bias}$	0.70	1.20	0.35	0.50	-0.15
$CH_4 + bC_{30}H_{62}$					
Coefficient	$x_1 = 0.0$	$x_1 = 0.0950$	$x_1 = 0.1977$	$x_1 = 0.3143$	$x_1 = 0.4052$
R_η	2.429×10^0	2.293×10^0	2.146×10^0	1.980×10^0	1.850×10^0
g_0	6.716×10^2	5.693×10^2	5.716×10^2	3.342×10^2	3.174×10^2
g_1	-1.106×10^0	-8.313×10^1	-1.119×10^0	-4.949×10^{-2}	-1.729×10^{-1}
g_2	1.095×10^{-3}	8.188×10^{-4}	1.281×10^{-3}	-1.941×10^{-4}	-5.389×10^{-6}
$10^2 \Delta_{AAD}$	3.78	5.12	5.94	8.45	12.33
$10^2 \Delta_{MAD}$	13.19	13.22	15.93	28.00	33.41
$10^2 \Delta_{bias}$	-0.72	1.16	1.45	-0.42	3.01

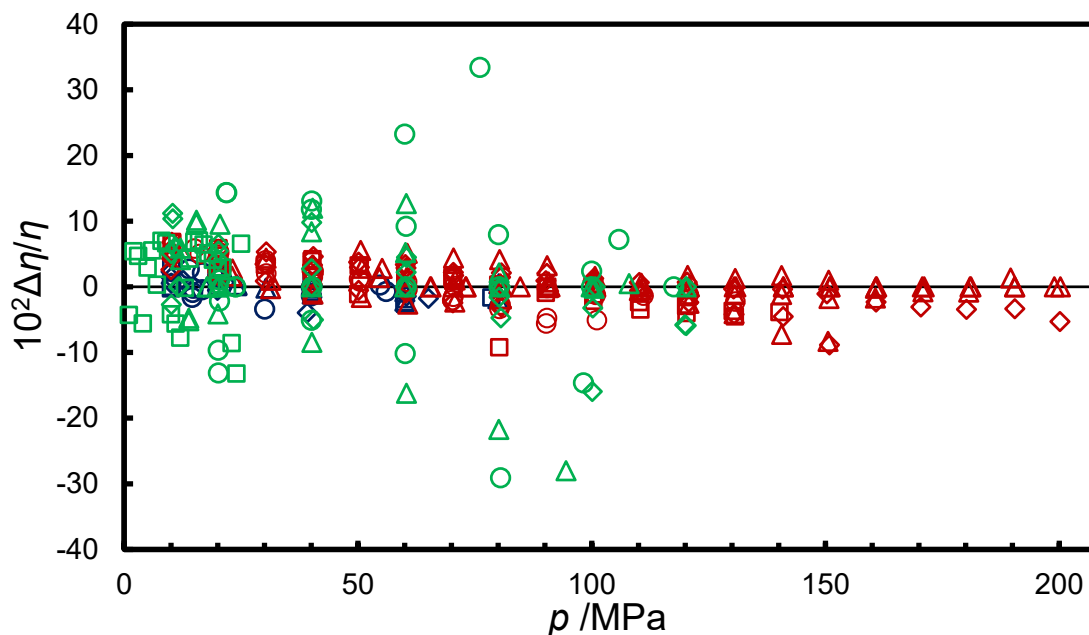


Figure 7.52: Relative deviations of equations 7.9 combined with equation 7.23 from the experimental viscosities of the three systems involving methane: $\square$, $x = 0.1$; $\diamond$, $x = 0.2$; $\triangle$, $x = 0.3$; and $\circ$, $x = 0.4$. A: blue symbols denote, $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$; B: red symbols denote, $\text{CH}_4 + \text{cC}_6\text{H}_{12}$ and C: green symbols denote $\text{CH}_4 + \text{bC}_{30}\text{H}_{62}$

From Figure 7.52, it was observed that the relative deviations of this scheme spanned from $(-4.0 \text{ to } 3.2) \%$ for the methane + hexadecane; $(-9.2 \text{ to } 5.8) \%$ for the methane + cyclohexane and $(-29.1 \text{ to } 33.4) \%$ for the methane + squalane systems respectively. While no particular trend with pressure was noticed, it was observed that the relative deviations of the methane + squalane systems were consistently larger than those of the methane + hexadecane and methane + cyclohexane at all compositions. Figure 7.53 presents the maximum absolute deviations $\Delta_{\text{MAD},\eta}$ of this scheme from the experimental data for range the range of mole fractions of methane investigated.

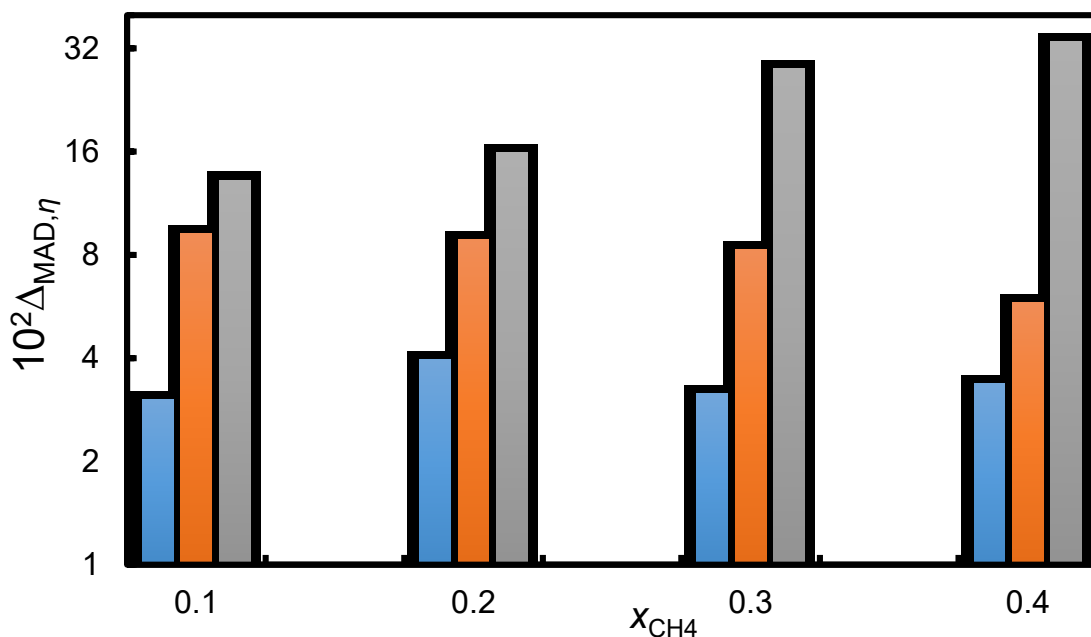


Figure 7.53: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of equation 7.9 combined with equation 7.23 from the experimental viscosity data for the three binary systems: A. ■, blue bars represent $CH_4 + cC_6H_{12}$; B. ■, orange bars represent $CH_4 + cC_6H_{12}$; and C. ■, grey bars represent $CH_4 + bC_{30}H_{62}$.

From Figure 7.53, it was observed that the $\Delta_{MAD,\eta}$ of the methane + squalane system increases systematically with increasing methane mole fractions. In contrast, a slightly decreasing trend in the $\Delta_{MAD,\eta}$ was observed for the system of methane + cyclohexane, whereas there is no any particular trend in $\Delta_{MAD,\eta}$ with methane mole fraction was noticed for the methane + hexadecane system.

In general, although this scheme is correlative in nature as it involved sets of fitting parameters for each individual mixture composition, however, it described the experimental data fairly well especially for the methane + hexadecane and methane + cyclohexane systems in which it reproduced the experimental data of the former system with $\Delta_{MAD,\eta}$ consistently less than 4 % and those of the latter system always less than 9 %. Furthermore, the correlations slightly over predicted the experimental data due to the positive biases $\Delta_{Bias,\eta}$ (0.1, 4.2 and 1.3)% obtained for the methane + hexadecane, methane + cyclohexane and methane + squalane respectively.

7.8.3 Vesovic-Wakeham (VW) model

In this work, the viscosities of the binary systems of methane + hexadecane and methane + cyclohexane were obtained from Nguyen, B^[65] via a private communications. Figures 7.54 and 7.55 present the deviation plots of the VW scheme from the experimental data for binary systems of methane + hexadecane and methane + cyclohexane respectively.

The methane +squalane system was not modelled using the VW scheme due to the reasons highlighted in the previous section.

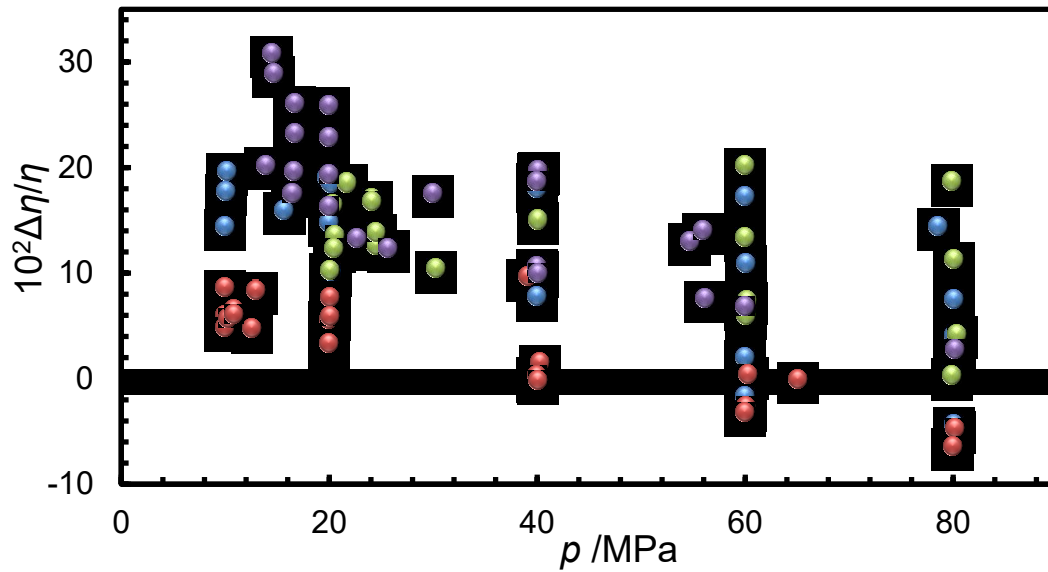


Figure 7.54: Fractional deviations of VW model from experimental data for binary mixtures of CH₄ + hexadecane as function of pressure: ●, $x = 0.1013$; ●, $x = 0.2021$; ●, $x = 0.2976$ and ●, $x = 0.3979$

It can be seen from Figure 7.53 that the relative deviations of the VW for the mixtures of methane + hexadecane are distributed within the range of (-6.4 to 28.9)%. Furthermore, it was also observed that the relative deviations increases as the mole fraction of methane increases except at the lowest methane mole fraction (i.e. $x = 0.1013$) at which some of the deviations are slightly higher than those at $x = 0.2021$. Moreover, this scheme predicted the experimental viscosities of these mixtures with average absolute deviations $\Delta_{AAD,\eta}$ of (11.5, 7.7, 13.0 and 17.3)% for the mole fractions of methane $x = (0.1013, 0.2021, 0.2976$ and $0.3979)$ respectively. Overall, the scheme over predict the experimental viscosities due to the strong positive biases $\Delta_{Bias,\eta}$ (10.9, 3.4, 13.0 and 17.3)% observed at the corresponding methane mole fractions $x = (0.1013, 0.2021, 0.2976$ and $0.3979)$.

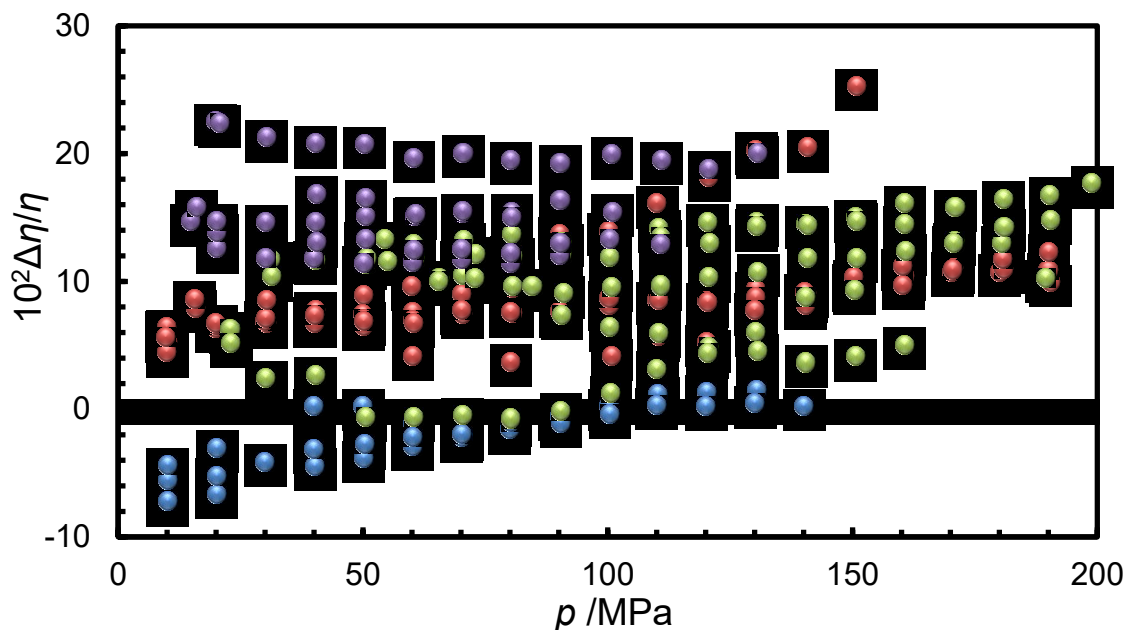


Figure 7.55: Fractional deviations of VW^[65] model from experimental data for binary mixtures of CH₄ + cyclohexane as function of pressure: ●, $x = 0.0992$; ●, $x = 0.2073$; ●, $x = 0.3031$ and ●, $x = 0.4020$

As can be seen from Figure 7.55 that the relative deviations of the VW for the mixtures of methane + cyclohexane are contained in the range of (-7.2 to 28.9)%. Again, similar increasing trend in the relative deviations with increasing methane mole fraction was observed, except at $x = 0.2073$ at which some of the deviations are higher than those at $x = 0.3031$. Furthermore, the VW scheme predicted the experimental viscosities of these mixtures with average absolute deviations $\Delta_{AAD,\eta}$ of (11.5, 7.7, 13.0 and 17.3)% for the mole fractions of methane $x = (0.0992, 0.2073, 0.3031 \text{ and } 0.4020)$ respectively.

In general, with the exception of the lowest methane mole fraction $x = 0.0992$ at which a negative relative bias $\Delta_{Bias,\eta} = -1.7\%$ was observed, the scheme again over predicted the experimental viscosities consistently for the rest of the three higher methane mole fractions with strong positive biases $\Delta_{Bias,\eta}$ (9.1, 10.1 and 15.7)% corresponding to methane mole fractions of $x = (0.2073, 0.3031 \text{ and } 0.4020)$ respectively. Figure 7.56 summarised the overall performance of this scheme in terms of three performance indicators namely; the maximum absolute deviations $\Delta_{MAD,\eta}$, the average absolute deviation $\Delta_{AAD,\eta}$, and the relative bias $\Delta_{Bias,\eta}$ for both binary systems.

Broadly, although the VW scheme over predicted the experimental viscosities of both systems due to the strong positive biases observed, however, the results are really satisfactory as the absolute average deviations $\Delta_{AAD,\eta}$ were always less than 12 % for the methane + hexadecane system, which is consistent with Ciotta^[4]'s observations of the $\Delta_{AAD,\eta} < 15\%$ in the case of CO₂ + hexadecane. In the case of methane + cyclohexane,

the VW predictions was even better as the $\Delta_{AAD,\eta}$ were consistently less than 10 % across all mole fractions of methane investigated in this work.

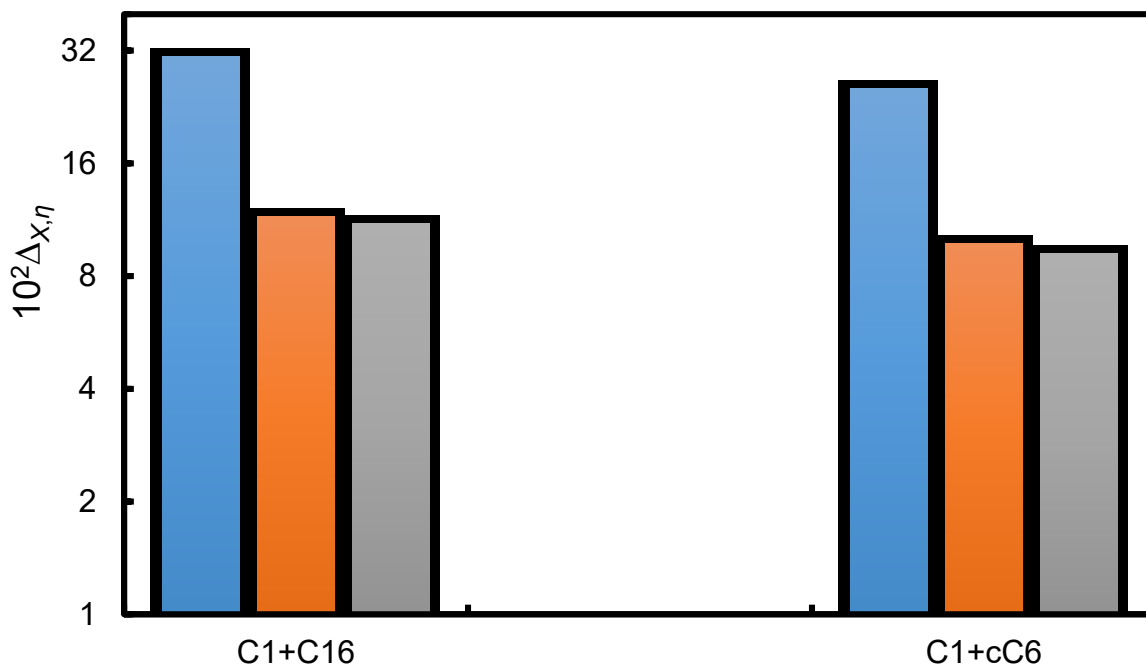


Figure 7.56: Deviations of VW^[65] model predictions of both methane + hexadecane and methane + cyclohexane mixtures from the experimental viscosities: A. ■, blue bars represent the $\Delta_{MAD,\eta}$; B. ■, orange bars represent $\Delta_{AAD,\eta}$; and C. ■, the grey bars represent the $\Delta_{Bias,\eta}$

7.8.4 Comparison between VW and extended hard sphere model

The predictive powers of the two models i.e. the extended hard sphere model and the VW model were tested by comparing their respective maximum absolute deviations $\Delta_{MAD,\eta}$, average absolute deviations $\Delta_{AAD,\eta}$; and relative biases $\Delta_{Bias,\eta}$ from the experimental data. Although, several mixing rules (both predictive and correlative) for the characteristic core volume of the mixtures were explored in the case of the extended hard sphere model, however in order to ensure consistency and fair comparison with the VW model, only the predictive mixing rules are considered for this purpose. Among the six predictive mixing rules tested with the extended hard sphere model, it was surprisingly discovered that the conventional/traditional linear mole-fraction-average rule gave better predictions in both systems and so, was selected for comparison with the VW model. Figures 7.57 and 7.58 compare the maximum absolute deviations $\Delta_{MAD,\eta}$, of both models from the experimental data at different mole fractions of methane.

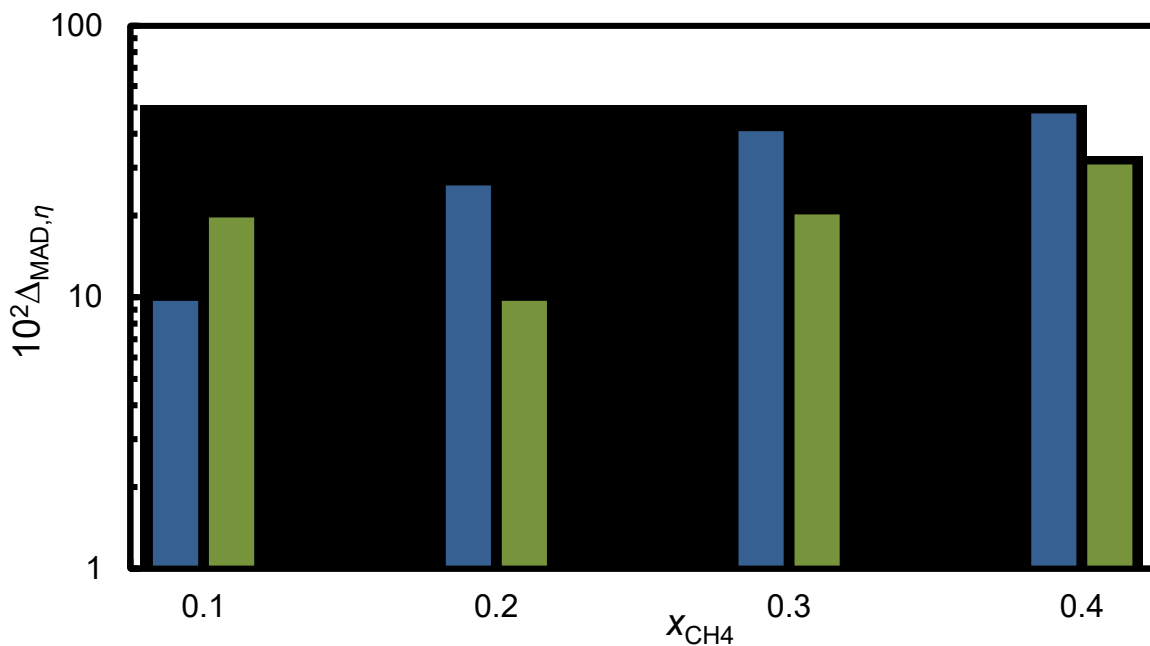


Figure 7.57: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of both extended hard sphere model equations 7.11 and VW^[65] model equations 4.46 from the experimental viscosity data for the methane + hexadecane system: A. ■, blue bars represent extended hard sphere model; B. ■, green bars represent the VW model.

It was observed from Figure 7.57 that the VW model produced relatively lower $\Delta_{MAD,\eta}$ compared to the extended hard sphere model, and this was observed across all the four methane mole fractions except at the lowest methane composition $x = 0.1013$ at which the $\Delta_{MAD,\eta}$ of the former is higher than that of the latter.

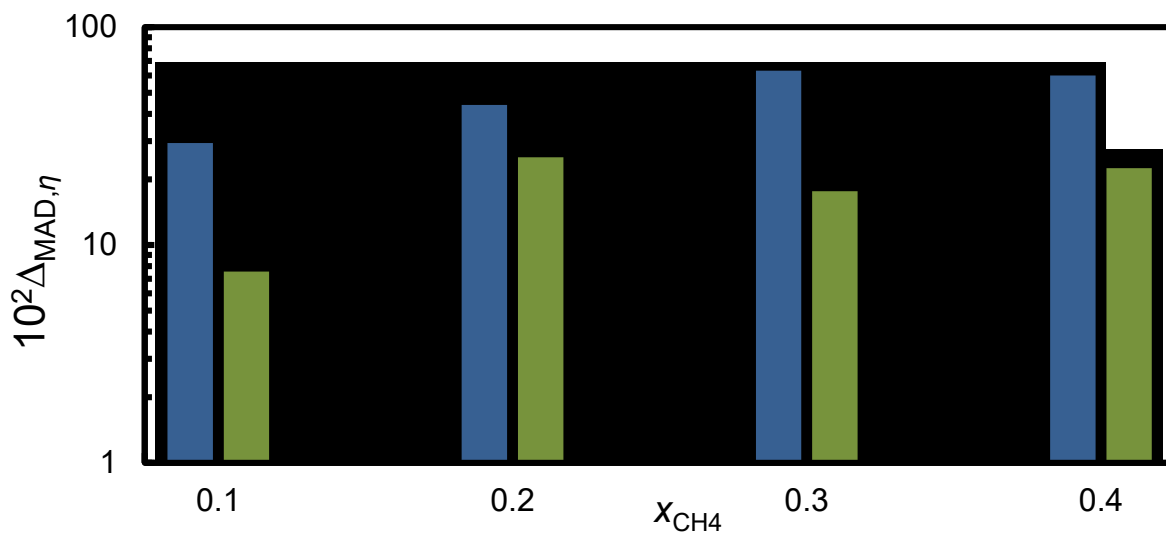


Figure 7.58: Maximum absolute relative deviation $\Delta_{MAD,\eta}$ of both extended hard sphere model equations 7.11 and VW^[65] model equations 4.46 from the experimental viscosity data for the methane + cyclohexane system: A. ■, blue bars represent extended hard sphere model; B. ■, green bars represent the VW model.

Again, it can be seen from Figure 7.58 that the VW model consistently gave better predictions in the range of methane mole fractions $x = (0.1 \text{ to } 0.4)$ investigated for this systems. In this range, it was observed that the $\Delta_{\text{MAD},\eta}$ of the extended hard sphere model are more than twice those of the VW except at $x = 0.2073$. The three performance indicators i.e. the $\Delta_{\text{MAD},\eta}$, $\Delta_{\text{AAD},\eta}$ and $\Delta_{\text{Bias},\eta}$ for both models are summarised in Table 7.20 for the two systems.

Table 7.20: The $10^2\Delta_{\text{MAD},\eta}$, $10^2\Delta_{\text{AAD},\eta}$ and $10^2\Delta_{\text{Bias},\eta}$ of the Extended HS and the VW^[65] Model for the $\text{CH}_4 + \text{n-C}_{16}\text{H}_{34}$ and $\text{CH}_4 + \text{c-C}_6\text{H}_{12}$ Systems

Extended Hard Sphere Model				VW ^[65] Model		
$\text{CH}_4 + \text{n-C}_{16}\text{H}_{34}$	$10^2\Delta_{\text{MAD},\eta}$	$10^2\Delta_{\text{AAD},\eta}$	$10^2\Delta_{\text{Bias},\eta}$	$10^2\Delta_{\text{MAD},\eta}$	$10^2\Delta_{\text{AAD},\eta}$	$10^2\Delta_{\text{Bias},\eta}$
$x = 0.1013$	9.7	3.8	-3.6	19.7	11.5	10.9
$x = 0.2021$	25.8	20.6	20.6	9.7	7.7	3.4
$x = 0.2976$	40.9	27.0	27.0	20.2	13.0	13.0
$x = 0.3979$	47.5	38.5	38.5	30.8	17.3	17.3
 $\text{CH}_4 + \text{c-C}_6\text{H}_{12}$						
$x = 0.0992$	29.4	23.2	23.2	7.6	2.5	-1.7
$x = 0.2073$	44.0	34.0	34.0	25.3	9.1	9.1
$x = 0.3031$	63.1	43.2	43.2	17.7	10.1	10.1
$x = 0.4020$	60.0	45.2	45.2	22.5	15.7	15.7

From Table 7.20, due to the positive biases observed at all compositions, it is evident that both models over-predicted the experimental viscosities of both systems except at two cases: (i). at methane mole fraction $x = 0.1013$ at which the extended hard sphere model under-predicted the experimental viscosities of the methane + hexadecane mixture and; (ii). at $x = 0.0992$ at which the VW model under-predicted the experimental viscosities of methane + cyclohexane mixture. Furthermore, it was observed that the VW model consistently gave lower average absolute deviations $\Delta_{\text{AAD},\eta}$ in both systems except at $x = 0.1013$. In general, considering the three performance indicators summarised in Table 7.21, the VW model gave better predictions compared to the extended hard sphere scheme and this, suggest that the former is more promising in predicting the viscosity of asymmetric mixtures.

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Summary and Conclusions

8.1 Introduction

The two broad aims of this project were: to measure the viscosity, and also the density, of representative asymmetric hydrocarbon mixtures; and to use the data obtained from these measurements to test the predictive performance of two promising theoretical models.

To achieve the first objective, several incremental improvements in the design of the existing vibrating-wire apparatus were implemented and the device was subsequently re-commissioned. Some of these improvements include enhancing the overall safety standards of the VWVD device. In this regards, two nitrogen purging units were incorporated in the fluid handling system in order to prevent the accumulation of highly flammable gases such as methane in the system in the event of leakage. In addition, the waste management of the system has been improved by extending and re-routing the gas outflow from the system to the central vent line in the laboratory. This is to comply with the basic safety requirement of ensuring that no dangerous gas was discharge to the laboratory environment. Furthermore, a new aluminium sinker with bigger dimensions than the previous one was designed and installed with the view to reducing the effective volume of the pressure cell to below 0.1 L such that it falls under Sound Engineering Practice according to the UK Pressure Equipment Regulations. Moreover, in order to facilitate study of mixtures of liquid with dissolved gasses, a new high-pressure magnetic circulation pump was designed and installed to overcome persistent problems experienced with the old pump. The new pump design not only eliminated the problems experienced previously, but also greatly enhanced the overall mixing efficiency of the system.

On the experimental side, the newly re-commissioned vibrating-wire device was used for simultaneous high-pressure, high-temperature measurements of density and viscosity on both pure compounds and mixtures of liquid with dissolved gases. The device was operated in absolute mode throughout this project. In this mode of operation, the properties of the centre-less ground tungsten wire (i.e. length and radius) as well as the properties of the suspended sinker (i.e. mass and volume) were independently determined via direct measurements rather than by calibration of the device. A large body of useful experimental viscosity and density data of both pure hydrocarbons and three binary asymmetric systems were collected over wide ranges of temperature, pressure and composition. The mixtures studied were methane + hexadecane, methane + cyclohexane and methane + squalane. Additional viscosity and density data on perfluoropolyether (also

known as krytox[®]) were also gathered over the entire working temperature and pressure range of the device, although the results of those measurements appear to be erroneous. The experimental data filled gaps in the literature, as data of methane + hydrocarbon mixtures, especially the higher-molecular weight hydrocarbons at high pressures, are poorly reported in the literature. The temperature and pressure covered in this work considerably extended the existing data for pure hexadecane. As expected, the addition of methane was shown to have a significant impact in reducing the viscosity of the mixtures, which was typical of all binary systems investigated. It is important to note, that this is the first time ever in our lab that the VWVD was operated in absolute mode.

The data were correlated both for density and viscosity using simple mathematical expressions that expressed both properties as functions of temperature and pressure. For density, correlations based on the modified Tait equation were developed for both pure components and each individual mixture of the three binary systems with relative uncertainties within the expanded uncertainty of the measurement, which is 0.2 % at 95 % confidence. Similarly, empirical correlations based on the Tait-Andrade equation were developed for the viscosities of the pure components as well as each individual mixture with relative uncertainties within the expanded uncertainty of the measurement, which is 2 % at 95 % confidence. These correlations allow the estimation of both properties to any state point within the temperature and pressure range investigated, and when applied with caution, could permit the extrapolation of data to other state points outside the stated range. Comparisons with some available literature data present satisfactory agreement mostly, within the mutual experimental uncertainties of our measurements and that of the data source concerned. For the krytox[®] however, large deviations between our data and some literature data were observed.

In an attempt to model the experimental viscosities of the three binary systems investigated, we explored the extended hard-sphere model in both predictive and correlative modes, with the molar core volumes of the mixtures expressed in different forms. First we tested two different forms of linear mixing rules; the conventional mole fraction- average rule and the one with and index parameter γ . We observed that the introduction of the index parameter produced slightly better estimations compared to the traditional mixing rule. Secondly, we tested several variations of a quadratic mixing rule including the situation where the core volume terms raised to one-third and two-third powers and with binary parameter I_{ij} expressed in different forms. In this approach, it was observed that making the binary parameter a linear function of temperature does not produce any significant improvement in the predictions in all cases. Finally, we considered the case in which the core volume of the mixtures treated as adjustable parameter and

optimised against experimental values for each individual composition of a given mixture. This approach described the experimental viscosity data with absolute relative deviations better than 5 % in the case of methane + hexadecane mixtures, less than 8 % for the methane + cyclohexane mixtures and about 30 % for the methane squalane mixtures, however this has become a correlative rather than a predictive approach.

The experimental viscosity results of two binary systems, were compared against the predicted values from the extended hard sphere and the VW model, and the predictive performance of these models were analysed in terms of three performance indicators (i.e. the $\Delta_{MAD,\eta}$, $\Delta_{AAD,\eta}$ and $\Delta_{Bias,\eta}$). The analysis revealed that the VW model consistently gave lower values for all the three quantities, with level of accuracy satisfactory for many industrial applications in most of the cases. For instance, as it was seen in the case of mixtures of methane + hexadecane the $\Delta_{MAD,\eta}$ from the VW model ranges from (10 to 31)%, whereas those from the extended hard sphere model ranges from (10 to 47)%. At this point, while both models could benefit from future improvements, however, we note that the VW model gave relatively better predictions especially for highly asymmetric systems and therefore, more likely to be recommended for predicting the viscosity of these type of mixtures. However, it is important to point out that the VW scheme also relies on the soundness of the correlations used in estimating the viscosities of the pure species, which often are not good or not available at all, for some really heavy components. For the HS model, better mixing rules are required for different types of fluid mixtures in the future. This highlights the need for further development of the fundamental theory of viscosity characteristics of highly asymmetric mixtures.

8.2 Future works

This project has been carried out with a view to provide useful experimental viscosity and density data on asymmetric hydrocarbon mixtures to fill the existing gaps in the literature. Considering the complexity preparing the mixtures concerned and, coupled with the limited time constrain, only some representative binary mixtures of aliphatic hydrocarbons with dissolved methane. Even in the aliphatic group, due to the complexity of the measurement process using the vibrating-wire device, only three binary systems were investigated. In this regard, further study of asymmetric mixtures involving representative components from other members of both higher molecular-weight aliphatic and aromatic compounds would enable better understanding of the viscosity behaviour of these mixtures. Similarly, to fully understand this property, asymmetric mixtures involving other lower-molecular weight gases such as (ethane, ethane, propane etc) including non-hydrocarbon ones such as CO₂ should be further studied.

The future of vibrating-wire viscometry is likely to require smaller sample volume due to safety concerns and the cost of the chemicals. In this work, efforts were made to reduce the effective volume of the pressure cell by designing a sinker with bigger dimensions in the existing VWVD device. However, this led to increase complexity in assembling and other persistent operational problems in working with the device. For instance, due to the size of the new sinker, the clearances between the sinker and the side-walls as well as the bottom of the pressure cell have been reduced significantly and so, any slight alteration from the vertical orientation could cause the sinker to touch the side of the cell, thus reducing the tension in the wire. Furthermore, due to the differences in the hardness of tungsten and aluminium, the wire, over long term usage especially at higher temperatures occasionally bites in to the aluminium clamp at the top of the sinker and this, caused the wire to slip and begin to touch the bottom of the pressure cell. This is also detrimental to the experiment, in that, it reduces the tension in the wire and ultimately affects the resonance frequency of the system. In addition, when the sinker is completely resting at the bottom of the cell, then the resonance frequency would never be detected in that situation. To resolve this problem, future design of the VWVD should explore the possibility of incorporating on to the sinker a clamp made from material with similar hardness and other mechanical properties as that of the vibrating wire itself. Alternatively, the vibrating wire could be clamped at both ends thereby avoiding the presence of the sinker in the vessel.

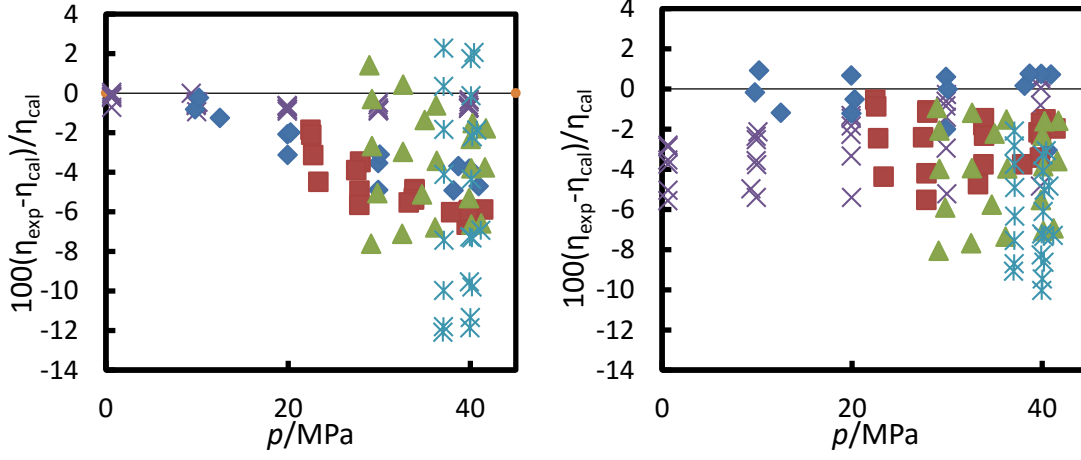
In view of the complexity in modelling the viscosity of asymmetric mixtures, future work in this regard should be aimed at understanding the viscosity of these mixtures from the molecular interaction of the smaller molecules around the bigger ones in the system. In the meantime however, some of the existing viscosity models could benefit from some useful empiricisms to minimise the discrepancies observed between the predicted values and the experimental data. For instance, the hard sphere model when used in such approach reproduces the experimental viscosity with satisfactory results with deviations acceptable for many engineering applications depending on the degree of asymmetry of the systems. The VW model has a strong grounding in kinetic theory proven for dense gases and super-critical fluids^[1]. The scheme however still have some challenges in implementation for dense fluids as it relies on the inputs of experimental viscosity data in form of correlations for the pure species, which are often not available for many dense fluid. This underscores the need for further experimental studies especially on complex fluids and their mixtures for the development and testing of both existing and new models.

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Appendix A: Comparative analysis of other methane + *n*-decane studies

2) Knapstad *et al.*^[1]

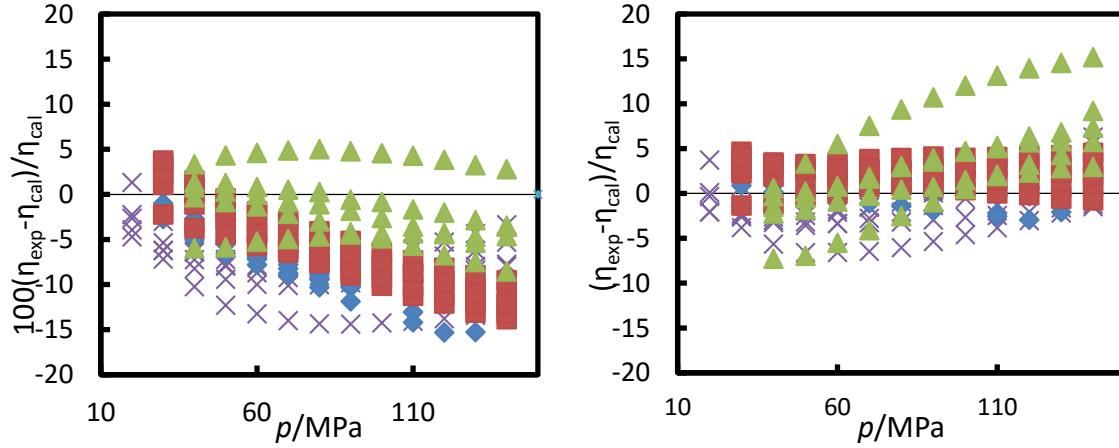


a) VW model^[2]

b) HS model

Figure A.1: Relative deviations of VW and HS models from Knapstad's results at temperatures between $293.15 \leq T/\text{K} \leq 430.15$ and $p/\text{MPa} \leq 40$. $\times$ $x_1 = 0$, $\diamond$ $x_1 = 0.3124$, $\blacksquare$ $x_1 = 0.5575$, $\blacktriangle$ $x_1 = 0.69$, and $\ast$ $x_1 = 0.8467$

3) Canet *et al.*^[3]



a) VW model^[2]

b) HS model

Figure A.2: Relative deviations of VW and HS models from Canet's results at temperatures between $293.15 \leq T/\text{K} \leq 373.15$ and $p/\text{MPa} \leq 140$. $\times$ $x_1 = 0.3124$, $\diamond$ $x_1 = 0.4867$, $\blacksquare$ $x_1 = 0.6$ and $\blacktriangle$ $x_1 = 0.7566$

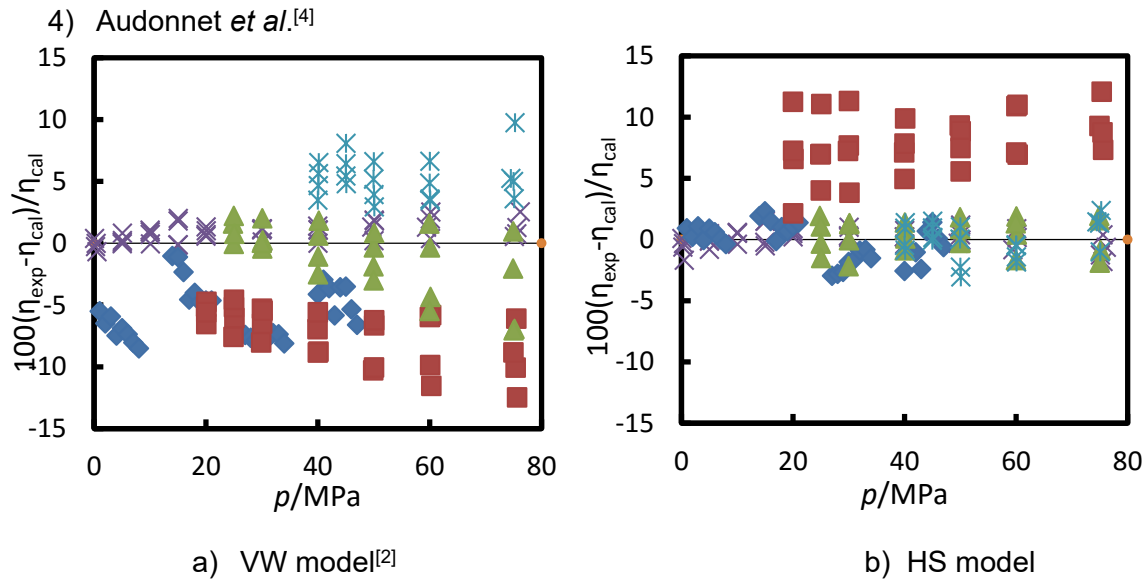


Figure A.3: Relative deviations of VW and HS models from Audonnet's results at temperatures in the range $303.15 \leq T / \text{K} \leq 393.15$ and $p / \text{MPa} \leq 75$. $\times$ $x_1 = 0$, $\blacklozenge$ $x_1 = 0.227$, $\blacksquare$ $x_1 = 0.41$, $\blacktriangle$ $x_1 = 0.601$ and $\ast$ $x_1 = 0.799$

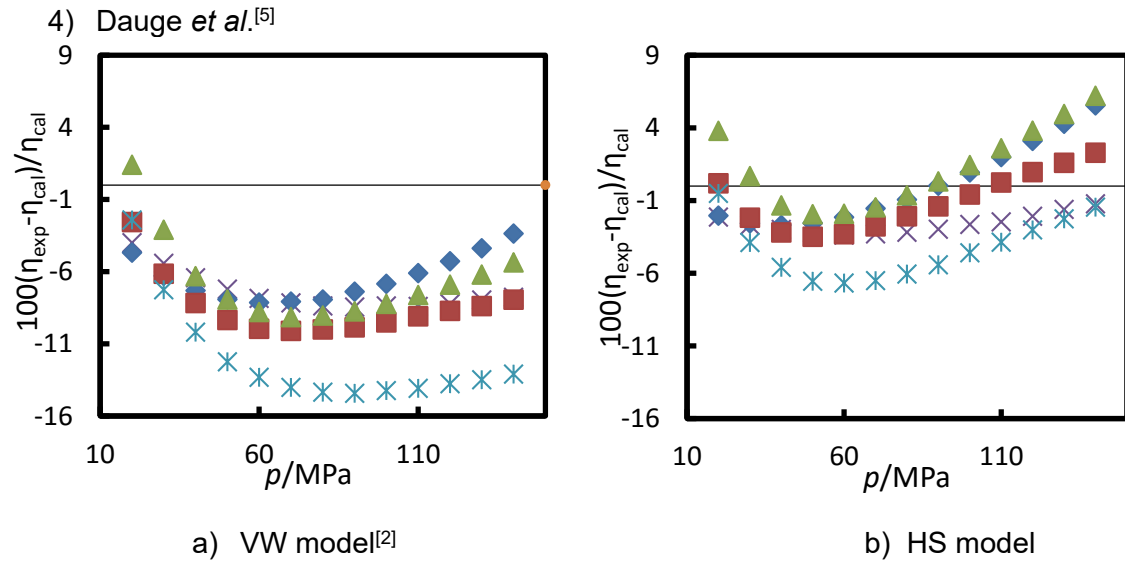


Figure A.4: Relative deviations of VW and HS models from Dauge's results at temperatures in the range $293.15 \leq T / \text{K} \leq 373.15$ and $p / \text{MPa} \leq 140$. $\times$ $T = 298.15 \text{ K}$, $\blacklozenge$ $T = 313.15 \text{ K}$, $\blacksquare$ $T = 333.15 \text{ K}$, $\blacktriangle$ $T = 353.15 \text{ K}$ and $\ast$ $T = 373.15 \text{ K}$

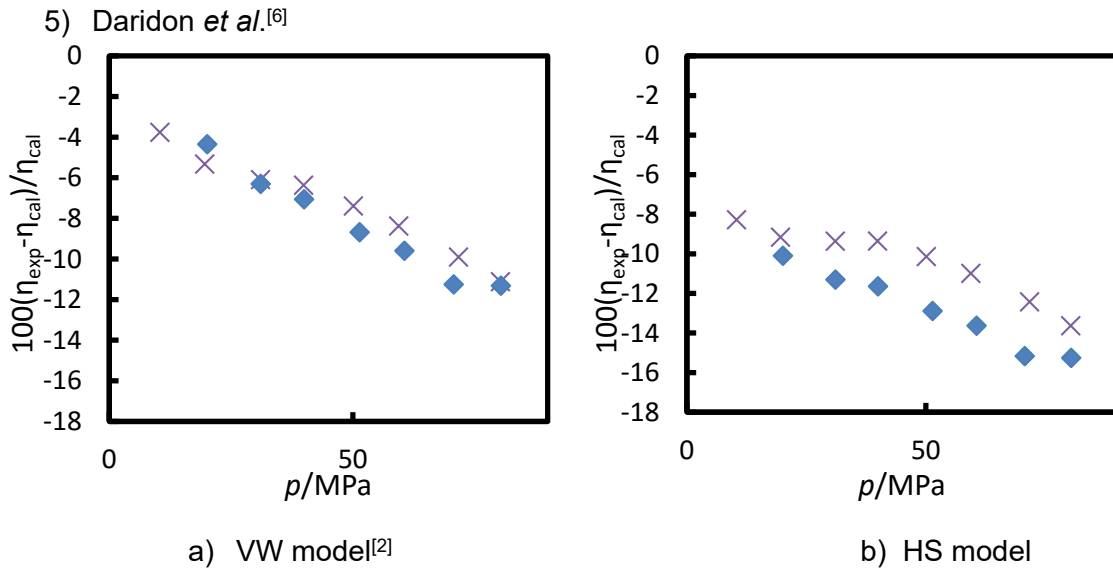


Figure A.5: Relative deviations of VW and HS models from Daridon's results at temperatures in the range $303.15 \leq T / \text{K} \leq 313.15$ and $p / \text{MPa} \leq 80$. $\times$ $x_1 = 0.227$, and $\diamond$ $x_1 = 0.3124$

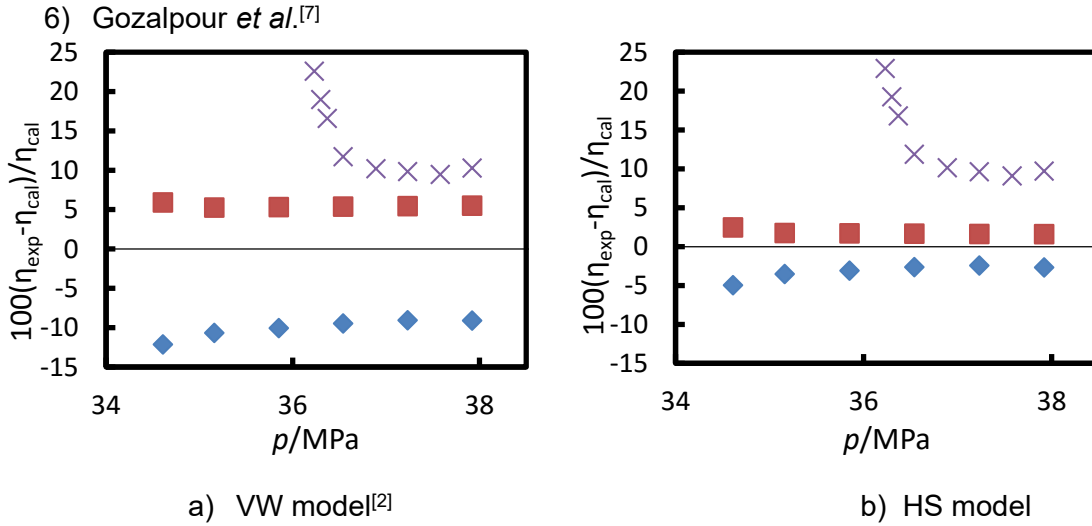


Figure A.6: Relative deviations of VW and HS models from Gozalpour's results at temperatures in the range $293.15 \leq T / \text{K} \leq 373.15$ and $p / \text{MPa} \leq 140$. $\times$ $x_1 = 0.8609$, $\diamond$ $x_1 = 0.9514$ and $\blacksquare$ $x_1 = 0.8064$

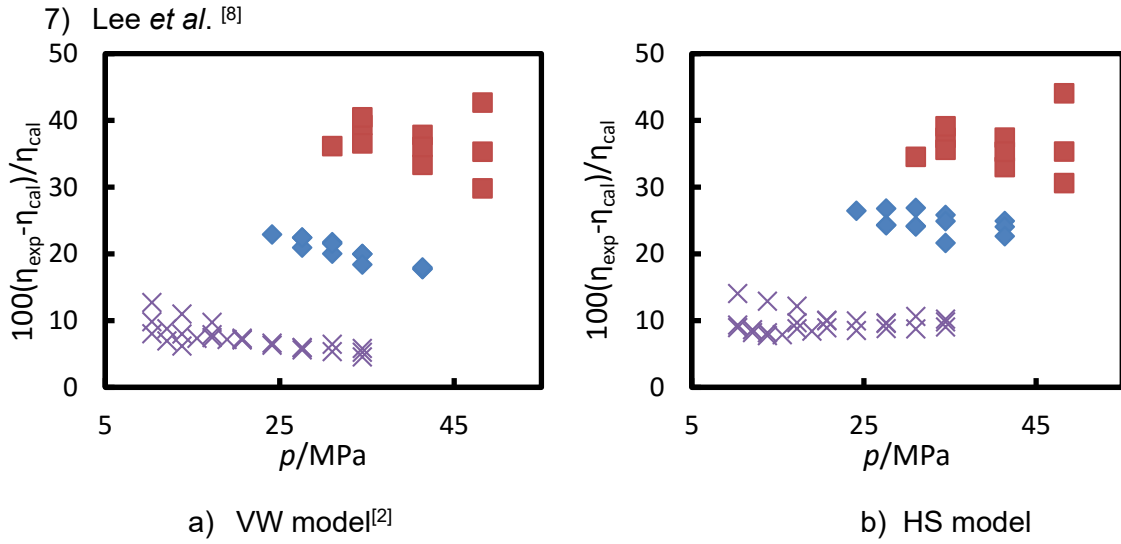


Figure A.7: Relative deviations of VW and HS models from LEE's results at temperatures in the range $310.93 \leq T / \text{K} \leq 400.00$ and pressures $10.342 \leq p / \text{MPa} \leq 48.263$. $\times$ $x_1 = 0.3$, $\diamond$ $x_1 = 0.5$ and $\blacksquare$ $x_1 = 0.7$

Appendix B: List of Experimental Results for Both Pure and Mixtures

Table B.1: Experimental Density ρ and Viscosity η of pure $n\text{-C}_{16}\text{H}_{34}$ at Temperatures T and Pressures p (b) obtained using VWVD

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.61$ K			$T = 398.28$ K		
0.97	768.9	3.143	1.05	700.3	0.697
10.34	774.7	3.562	21.19	719.6	0.879
20.57	780.8	4.041	41.29	735.3	1.082
30.37	785.9	4.588	59.99	747.8	1.267
			80.67	759.3	1.498
			94.51	770.3	1.774
$T = 323.22$ K			$T = 423.31$ K		
0.99	752.4	1.878			
20.96	764.8	2.429			
42.10	777.2	3.007	1.46	682.9	0.554
61.17	787.4	3.666	20.61	704.4	0.699
81.17	796.0	4.471	40.76	721.8	0.853
			60.12	735.2	1.012
$T = 348.20$ K			80.99	748.2	1.189
0.61	734.8	1.275	92.02	758.3	1.369
20.37	749.8	1.595			
40.78	762.9	1.970			
62.00	773.9	2.398			
80.38	783.3	2.813	1.23	663.8	0.445
95.57	793.5	3.361	20.75	688.9	0.571
			40.68	707.8	0.702
$T = 373.25$ K			60.65	723.1	0.831
1.37	717.7	0.926	80.72	736.2	0.970
19.85	733.7	1.148	99.65	747.8	1.102
40.19	748.6	1.399			
59.97	760.4	1.692			
81.31	771.4	1.995	1.40	645.2	0.367
94.98	781.3	2.355	21.26	674.3	0.478
			41.04	694.7	0.590
			61.19	711.3	0.706
			81.71	725.7	0.815
			92.30	738.3	0.939

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$ and $U(\eta) = 0.02\eta$ with a coverage factor k of 2

Table B. 2: Experimental Density ρ and Viscosity η of $x\text{CH}_4(1)+(1-x)\text{C}_{16}\text{H}_{34}(2)$, at Temperatures T , Pressures p , and Composition $x_1 = 0.1013$ obtained using VWVD

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.15$ K			$T = 323.22$ K		
10.20	781.5	3.304	10.10	764.9	1.993
19.80	786.6	3.687	20.20	771.1	2.205
			40.00	781.9	2.690
			60.00	791.6	3.255
			78.60	799.8	3.927
$T = 373.26$ K			$T = 423.31$ K		
10.00	732.8	0.967	15.70	708.0	0.611
20.20	741.0	1.112	20.00	712.4	0.643
40.10	755.1	1.334	40.00	730.1	0.816
60.10	767.1	1.571	60.00	744.5	1.004
80.10	777.7	1.897	80.10	757.0	1.133
$T = 473.17$ K					
40.00	703.2	0.591			
60.00	719.3	0.687			
80.10	732.8	0.794			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.3: Experimental Density ρ and Viscosity η of $x\text{CH}_4$ (1)+ $(1-x)\text{C}_{16}\text{H}_{34}$ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.2021$, obtained using VWVD

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.22$ K			$T = 323.32$ K		
10.00	775.2	3.308	10.00	756.9	1.901
20.00	781.2	3.742	20.10	763.7	2.147
			39.10	775.2	2.576
$T = 373.20$ K			$T = 423.24$ K		
10.00	721.2	0.926	10.30	686.7	0.557
12.60	723.4	0.951	10.90	687.4	0.556
20.00	729.6	1.037	20.00	697.2	0.625
40.30	744.5	1.270	40.00	715.4	0.762
60.30	757.2	1.521	60.10	730.4	0.912
65.10	759.9	1.586	80.20	743.2	1.067
			10.90	687.1	0.557
$T = 473.36$ K					
13.00	656.9	0.387			
20.10	666.7	0.425			
40.10	688.5	0.530			
60.00	705.9	0.627			
80.00	720.4	0.732			
13.00	657.2	0.388			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.4: Experimental Density ρ and Viscosity η of $x\text{CH}_4$ (1) + $(1-x)\text{C}_{16}\text{H}_{34}$ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.2976$, obtained using VWVD

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.20$ K			$T = 323.23$ K		
20.10	782.5	3.712	20.40	767.9	2.146
30.30	788.5	4.196	21.70	768.8	2.151
			40.20	780.0	2.597
			60.00	790.6	3.162
$T = 373.41$ K			79.90	800.0	3.859
24.10	739.3	1.038	21.70	768.8	2.147
40.10	750.6	1.222			
60.00	762.8	1.465			
80.10	773.7	1.749	$T = 423.58$ K		
24.10	739.3	1.040	20.60	703.6	0.606
			22.80	705.4	0.618
$T = 473.40$ K			40.10	720.5	0.734
24.50	676.3	0.431	60.20	735.1	0.873
40.10	693.3	0.501	80.40	747.6	1.030
60.10	710.8	0.600	20.50	703.5	0.612
79.90	725.2	0.717			
24.50	676.6	0.427			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.5: Experimental Density ρ and Viscosity η of $x\text{CH}_4$ (1)+ $(1-x)\text{C}_{16}\text{H}_{34}$ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.3979$, obtained using VWVD

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.33$ K			$T = 323.26$ K		
13.90	780.8	3.321	14.50	766.4	1.887
20.00	783.7	3.548	14.70	766.5	1.918
30.00	788.0	3.938	20.00	769.2	2.058
			40.10	778.6	2.560
$T = 373.47$ K			$T = 423.94$ K		
			16.50	698.8	0.565
16.70	734.8	0.921	16.60	698.8	0.555
16.70	734.8	0.942	20.00	701.8	0.587
20.00	736.9	0.970	40.00	717.7	0.717
40.00	748.9	1.170	56.20	728.6	0.822
54.70	756.7	1.365			
56.00	757.3	1.364			
$T = 473.68$ K					
22.70	672.9	0.420			
25.70	676.5	0.435			
40.10	692.3	0.502			
60.00	710.0	0.596			
80.20	724.9	0.704			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Expanded uncertainties are $u(T) = 0.02 \text{ mK}$; $u(p) = 0.2 \text{ MPa}$; $U(p) = 0.003p$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.7: Experimental Density ρ and Viscosity η of CH₄ (1) + bC₃₀H₆₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.1977$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 303.49$ K			$T = 398.28$ K		
10.1	804.6	27.663	11.0	745.6	2.151
20.0	810.3	34.238	20.2	753.2	2.438
40.5	821.6	50.343	40.1	768.3	3.140
10.1	806.3	27.259	60.3	780.6	4.013
			80.6	792.7	4.886
			100.2	801.2	6.057
			120.2	809.7	7.303
			11.0	745.8	2.152
$T = 348.17$ K			$T = 448.34$ K		
10.4	776.3	5.656	11.6	717.1	1.172
20.2	784.1	6.504	20.2	725.6	1.312
40.1	794.9	8.954	40.1	742.9	1.687
60.4	806.5	11.763	60.1	757.3	2.067
80.2	816.6	15.112	80.5	769.9	2.492
100.1	827.6	19.139	100.8	781.9	2.968
119.9	833.2	25.644	120.2	791.3	3.496
10.4	776.6	5.644	11.8	716.7	1.174

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.8: Experimental Density ρ and Viscosity η of CH₄ (1) + bC₃₀H₆₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.3143$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 303.52$ K			$T = 398.43$ K		
12.0	807.7	28.479	15.4	750.5	2.316
20.0	812.6	33.148	20.5	754.5	2.480
40.3	819.5	50.339	40.1	768.6	3.189
60.3	828.1	74.638	60.2	781.4	3.996
12.0	807.2	28.447	80.2	792.5	4.942
			100.5	802.2	6.068
			108.0	805.4	6.608
			15.5	750.3	2.309
$T = 348.35$ K			$T = 448.58$ K		
13.8	780.2	5.967	17.7	724.1	1.281
20.0	783.7	6.606	20.1	726.3	1.313
40.2	795.7	8.876	40.1	743.4	1.682
60.4	806.9	11.662	60.0	758.0	2.068
80.1	816.3	15.181	80.3	770.7	2.52
94.5	822.9	18.258	99.9	781.6	2.977
13.8	779.9	5.939	120.2	791.0	3.536
			17.7	723.1	1.275

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.9: Experimental Density ρ and Viscosity η of CH₄ (1) + bC₃₀H₆₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.4052$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 303.47$ K			$T = 398.09$ K		
20.1	812.9	31.723	21.8	754.2	2.438
40.1	816.6	48.323	40.0	767.9	3.043
60.0	822.4	70.822	60.3	780.7	3.824
76.1	825.7	95.211	80.1	791.4	4.760
20.1	812.2	31.710	100.0	801.9	5.726
			105.8	803.1	6.210
			21.9	754.4	2.443
$T = 348.28$ K			$T = 448.22$ K		
			23.8	728.5	2.438
20.4	783.5	6.355	40.2	742.3	3.043
40.1	795.2	8.549	60.3	757.0	3.824
60.1	805.6	11.163	80.2	768.7	4.76
80.5	817.4	14.039	99.9	779.9	5.726
98.2	821.6	18.341	117.5	788.8	6.21
20.4	782.4	6.352	23.8	727.8	2.443

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.10: Experimental Density ρ and Viscosity η of pure cyclohexane, at Temperatures T , Pressures p .

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.76$ K			$T = 348.50$ K		
0.2	773.0	0.895	0.1	725.4	0.444
19.6	788.3	1.159			
$T = 323.63$ K			$T = 423.71$ K		
0.1	748.2	0.615	52.4	719.3	0.398
10.3	758.8	0.696	60.3	726.6	0.431
20.0	767.1	0.792			
30.1	775.1	0.887			
38.4	781.6	0.953			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$ with a coverage factor k of 2

Table B.11: Experimental Density ρ and Viscosity η of CH₄ (1) + cC₆H₁₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.0992$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.23$ K			$T = 373.23$ K		
10.2	768.4	0.932	10.2	695.7	0.352
20.2	776.9	1.055	20.3	709.1	0.394
30.1	784.6	1.164	40.1	730.0	0.489
40.1	792.2	1.267	50.4	738.8	0.537
50.1	798.5	1.416	60.2	746.9	0.586
60.2	804.3	1.597	70.3	754.3	0.638
70.4	809.9	1.790	80.2	761.2	0.688
80.2	817.2	1.877	90.5	767.9	0.749
$T = 323.23$ K			100.5	774.0	0.805
			110.1	779.8	0.863
10.2	742.4	0.617	120.2	785.3	0.930
20.2	751.7	0.690	130.2	788.7	0.972
40.3	768.1	0.853	140.2	792.1	1.021
50.2	775.1	0.938			
60.2	781.9	1.029			
70.2	788.4	1.131			
80.0	794.3	1.236			
90.2	800.2	1.349			
100.4	805.7	1.470			
110.4	811.0	1.598			
120.3	815.8	1.738			
130.6	818.4	1.818			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.12: Experimental Density ρ and Viscosity η of CH₄ (1) + cC₆H₁₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.2073$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.25$ K			$T = 423.32$ K		
10.2	748.5	0.670	15.9	631.0	0.192
20.1	757.5	0.748	20.1	639.6	0.206
30.4	765.8	0.839	30.2	656.9	0.233
40.4	773.5	0.933	50.2	683.0	0.289
50.2	780.2	1.026	60.4	693.8	0.317
60.1	786.6	1.133	70.2	703.1	0.342
70.5	793.2	1.242	80.3	711.7	0.372
80.5	798.7	1.362	90.3	719.6	0.402
90.2	803.9	1.485	100.4	727.1	0.430
100.3	808.9	1.627	110.6	734.0	0.463
110.2	814.0	1.761	120.5	740.2	0.496
120.8	819.1	1.912	130.4	746.2	0.528
130.4	823.6	2.055	140.4	752.0	0.561
141.0	827.8	2.234	150.3	757.5	0.593
150.9	832.4	2.361	160.4	762.6	0.630
$T = 323.28$ K			170.7	767.9	0.662
10.0	722.7	0.470	180.9	772.8	0.701
20.1	732.9	0.525	190.1	777.0	0.737
30.2	742.3	0.585	15.7	630.4	0.190
40.2	750.8	0.651	$T = 473.40$ K		
50.1	758.8	0.718	30.4	613.7	0.167
60.3	766.5	0.797	40.2	631.3	0.189
70.3	774.0	0.876	50.3	645.4	0.209
80.7	781.9	0.982	60.3	656.9	0.233
10.1	723.2	0.481	80.3	677.3	0.274
$T = 373.24$ K			100.9	696.0	0.320
10.1	672.2	0.275	110.5	704.3	0.340
20.2	687.2	0.312	120.3	711.1	0.364
30.1	699.6	0.349	130.2	718.5	0.382
40.3	710.4	0.388	140.5	725.0	0.406
50.3	719.9	0.426	150.4	732.4	0.429
60.3	728.3	0.466	160.3	738.2	0.452
70.4	736.4	0.507	170.5	743.7	0.480
80.7	743.8	0.551	180.7	749.0	0.504
90.4	750.3	0.595	190.2	753.9	0.528
100.4	756.8	0.640			
110.2	762.6	0.685			
120.4	768.3	0.737			
130.4	773.7	0.784			
140.8	779.0	0.843			

150.3	784.0	0.898
160.8	789.3	0.958
170.4	794.5	1.027
180.1	797.7	1.074
190.5	802.2	1.153
200.1	806.4	1.210
9.9	672.6	0.278

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.13: Experimental Density ρ and Viscosity η of CH₄ (1) + cC₆H₁₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.3031$

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.27$ K			$T = 423.41$ K		
23.0	732.1	0.588	65.7	673.3	0.276
30.3	738.7	0.660	70.4	677.8	0.286
40.4	746.4	0.725	73.1	682.0	0.292
50.6	753.9	0.827	80.8	688.7	0.310
60.5	759.4	0.892	90.7	697.1	0.334
70.4	765.8	0.977	100.6	704.6	0.359
80.3	772.0	1.075	110.9	712.1	0.381
90.5	777.8	1.170	120.9	718.6	0.408
100.7	783.3	1.262	130.5	724.8	0.430
110.2	788.5	1.352	141.0	730.9	0.458
120.8	794.1	1.466	151.0	736.7	0.486
130.4	798.3	1.562	160.8	742.0	0.509
140.6	804.1	1.694	171.1	747.1	0.540
150.5	808.6	1.834	180.9	752.1	0.568
23.2	731.8	0.592	190.4	756.7	0.597
$T = 323.15$ K			199.0	760.8	0.621
31.3	717.5	0.458	65.5	673.1	0.276
40.4	725.6	0.500	73.0	680.4	0.293
50.7	733.9	0.551	$T = 473.53$ K		
60.6	741.3	0.599	84.7	660.7	0.243
70.7	748.5	0.661	91.1	666.8	0.256
80.7	754.9	0.725	100.9	675.4	0.273
90.7	760.8	0.801	110.9	683.6	0.292
100.6	766.7	0.877	120.8	691.2	0.310
110.6	772.1	0.952	130.8	698.3	0.329
120.5	777.0	1.039	141.0	705.1	0.347
130.7	782.2	1.123	150.9	711.3	0.368
140.6	786.7	1.215	161.0	717.2	0.388
150.7	791.3	1.302	170.7	722.8	0.408
160.7	795.6	1.385	181.1	728.4	0.427
31.4	717.2	0.462	190.5	733.3	0.447

	200.2	737.9	0.471
$T = 373.24 \text{ K}$			
50.8	695.8	0.347	
54.6	699.6	0.355	
60.5	705.2	0.376	
70.8	713.7	0.408	
80.5	721.2	0.439	
90.8	728.3	0.476	
100.6	735.0	0.512	
110.6	741.1	0.544	
120.5	747.1	0.581	
130.6	752.8	0.622	
140.6	757.9	0.663	
150.7	763.7	0.710	
160.7	769.4	0.767	
170.9	773.8	0.822	
180.6	777.8	0.868	
189.6	781.6	0.936	
55.2	699.5	0.360	

Expanded uncertainties are $u(T) = 0.02 \text{ mK}$; $u(p) = 0.2 \text{ MPa}$; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B.14: Experimental Density ρ and Viscosity η of CH₄ (1) + cC₆H₁₂ (2), at Temperatures T , Pressures p , and Composition $x_1 = 0.4020$

p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	p/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$
$T = 298.11 \text{ K}$			$T = 423.28 \text{ K}$		
20.3	668.8	0.327	40.6	584.1	0.156
30.3	680.0	0.364	50.6	600.7	0.173
40.1	689.8	0.399	60.5	614.5	0.191
50.2	698.6	0.436	70.3	626.3	0.207
60.2	706.8	0.473	80.3	636.9	0.224
70.2	714.8	0.513	90.4	646.6	0.239
80.3	722.6	0.560	100.5	655.4	0.255
90.3	730.3	0.608	110.9	663.6	0.273
20.3	670.1	0.327			
$T = 323.18 \text{ K}$			$T = 473.41 \text{ K}$		
15.0	644.5	0.254	40.6	542.6	0.114
20.2	652.1	0.270	50.7	563.8	0.130
30.3	665.4	0.302	60.9	580.8	0.146
40.5	676.6	0.333	70.4	594.7	0.159
50.7	686.5	0.363	80.5	607.2	0.173
60.6	695.2	0.394			
70.4	703.1	0.425			
80.5	710.8	0.459			
90.4	718.0	0.491			

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101.1	724.6	0.532
16.1	645.7	0.254

$T = 373.23 \text{ K}$

20.0	599.2	0.164
30.4	618.7	0.189
40.4	633.5	0.211
50.4	646.0	0.232
60.5	656.8	0.255
70.6	666.4	0.275
80.3	674.9	0.297
90.4	682.8	0.319
100.9	690.4	0.340
111.1	697.3	0.364
120.8	703.3	0.388
130.7	709.4	0.408
20.8	600.9	0.166

Expanded uncertainties are $u(T) = 0.02 \text{ mK}$; $u(p) = 0.2 \text{ MPa}$; $U(\rho) = 0.003\rho$; $U(\eta) = 0.02\eta$; and $u(x) = 0.002x_1$ with a coverage factor k of 2

Table B 15: Experimental Density ρ and Viscosity η of krytox® at Temperatures T and Pressures p , - First VWVD datasets

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.49$ K			$T = 398.36$ K		
0.12	1856.1	53.171	0.15	1635.6	2.527
25.47	1922.6	148.070	25.10	1735.6	5.662
			50.18	1796.2	9.894
$T = 323.53$ K			75.10	1838.9	16.096
1.24	1798.1	17.227	100.21	1872.8	25.202
25.05	1871.5	40.830	125.32	1910.9	36.581
50.20	1914.8	81.653	150.14	1941.0	49.627
75.16	1953.4	135.759	175.09	1975.4	69.260
			200.22	1993.8	96.847
$T = 348.21$ K			$T = 423.32$ K		
0.20	1746.5	7.755	0.10	1579.1	1.690
25.30	1812.1	17.119	25.00	1693.4	3.673
50.10	1862.5	31.726	50.10	1755.3	6.340
75.10	1912.3	55.594	75.10	1800.3	9.845
100.20	1950.8	91.161	100.10	1838.3	14.808
125.50	1982.2	148.333	125.10	1867.7	21.810
$T = 373.84$ K			150.10	1894.6	30.080
0.10	1690.9	4.174	175.10	1922.1	41.380
25.00	1772.8	8.967	200.00	1950.2	53.732
50.03	1822.1	16.487	$T = 448.33$ K		
75.20	1862.0	27.669	25.10	1649.3	2.641
100.10	1900.9	43.982	50.11	1719.1	4.427
125.26	1945.1	68.796	75.14	1770.9	6.868
150.87	1973.9	93.296	100.14	1811.6	10.000
			125.01	1844.9	14.053
			150.08	1877.3	19.604
			175.62	1906.2	25.446
			200.07	1926.5	34.595

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$ and $U(\eta) = 0.02\eta$ with a coverage factor k of 2

Table B.16: Experimental Density ρ and Viscosity η of krytox[®] at Temperatures T and Pressures p , Second VWVD datasets

p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)	p /MPa	ρ /(kg·m ⁻³)	η /(mPa·s)
$T = 298.25$ K			$T = 423.40$ K		
0.1	1854.2	49.723	0.2	1615.7	1.826
5.2	1858.8	62.114	25.2	1658.2	3.611
10.2	1865.2	76.083	50.2	1686.5	6.136
15.1	1870.5	94.056	75.2	1704.0	9.815
			100.3	1712.6	14.719
$T = 323.42$ K			125.0	1725.0	21.665
0.2	1807.1	17.331	150.4	1734.3	30.605
25.0	1831.0	40.021	175.6	1744.9	41.239
50.0	1849.3	79.340	200.5	1753.7	52.520
$T = 348.22$ K			$T = 448.37$ K		
0.2	1758.3	7.926	0.2	1562.8	1.388
25.3	1791.6	17.545	25.5	1612.3	2.592
49.9	1807.8	33.461	50.4	1641.2	4.283
75.1	1826.9	59.048	75.3	1658.9	6.698
100.3	1838.6	96.276	100.3	1668.6	10.037
$T = 373.28$ K			125.1	1682.4	14.597
0.1	1709.3	4.443	150.3	1692.3	20.582
25.1	1743.9	8.838	175.2	1701.1	27.336
50.2	1767.7	15.800	200.2	1708.2	35.378
74.9	1786.4	27.283	$T = 473.53$ K		
100.2	1800.4	44.866	0.1	1514.3	1.131
125.1	1809.9	67.918	10.1	1542.1	1.381
150.1	1816.0	94.925	25.2	1568.5	1.928
$T = 398.21$ K			50.4	1593.5	3.163
0.1	1663.7	2.766	75.2	1608.1	4.919
25.1	1700.1	5.252	100.4	1622.6	7.376
50.1	1729.2	9.279	125.1	1634.3	10.495
75.2	1742.9	15.300	150.2	1644.6	14.412
100.3	1754.3	23.834	175.1	1655.8	19.588
125.3	1768.6	36.149	200.8	1663.0	24.547
150.3	1777.1	51.964			
175.1	1783.8	68.554			
200.8	1794.4	87.054			

Expanded uncertainties are $u(T) = 0.02$ mK; $u(p) = 0.2$ MPa; $U(\rho) = 0.003\rho$ and $U(\eta) = 0.02\eta$ with a coverage factor k of 2

Table B.17: Calibration data for the pressure transducer STI GT1600: (a) calibration from this work and (b) Manufactures calibration data.

(a)

p /MPa	v_{output} / volts	v_{best} /volts	Δv /volts	$10^2 \Delta v/v$
0.00	0.007	0.007	0.000	0.000
10.05	0.486	0.486	-0.003	0.000
20.04	0.962	0.962	-0.003	0.000
30.03	1.438	1.438	-0.012	-0.001
40.03	1.914	1.915	-0.011	-0.001
50.03	2.391	2.391	-0.008	0.000
60.02	2.867	2.867	-0.004	0.000
70.01	3.343	3.343	-0.020	-0.001
80.01	3.819	3.819	-0.014	-0.001
90.00	4.295	4.295	-0.018	-0.001
100.00	4.771	4.771	0.000	0.000
90.01	4.295	4.295	0.002	0.000
80.01	3.819	3.819	-0.004	0.000
70.02	3.343	3.343	0.000	0.000
60.03	2.867	2.867	0.006	0.000
50.03	2.391	2.391	0.002	0.000
40.04	1.915	1.915	0.009	0.000
30.04	1.439	1.438	0.008	0.000
20.05	0.962	0.962	0.007	0.000
10.05	0.486	0.486	0.007	0.000

(b)

Step %	p /MPa	v_{output} / volts	v_{best} /volts	Δv /volts	$10^2 \Delta v/v$
0	0.00	0.007	0.007	0.000	0.000
20	41.37	1.002	1.003	-0.001	-0.020
40	82.74	1.998	1.999	-0.001	-0.020
60	124.11	2.993	2.994	-0.001	-0.020
80	165.47	3.989	3.990	-0.001	-0.020
100	206.84	4.985	4.985	0.000	0.000
80	165.47	3.991	3.990	0.001	0.020
60	124.11	2.996	2.994	0.002	0.040
40	82.74	2.000	1.999	0.001	0.020
20	41.37	1.004	1.003	0.001	0.020
0	0	0.007	0.007	0.000	0.000

DESIGN REPORT FOR 200 MPa PRESSURE VESSEL



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9th April, 2013

Summary

This report presents an appraisal of the design of a pressure vessel to be used with a vibrating-wire instrument in a system for measuring the viscosity and density of fluids. The vessel, which was initially manufactured in 2007, consists of a blind hollow cylinder fitted with a plug closure and screw cap. The overall external dimensions are 79 mm diameter and 398 mm height; the internal dimensions are diameter 31.75 mm and depth 287.8 mm. Taking into account the displacement of the vibrating-wire sensor to be fitted within the vessel, the net internal volume is found to be 0.095 L. The design, construction and commissioning of this vessel therefore falls outside the scope of the Pressure Equipment Regulations, and an approach based on Sound Engineering Practice was followed. In this approach, the pressure loading and the various dimensions of the vessel were determined by stress analysis (design by formula). The maximum working pressure and temperature of the vessel are 200 MPa and 200°C, respectively, and the stress analysis was performed at the maximum pressure possible (test pressure). Moreover, stress concentration around the neck and base of the vessel was analysed to evaluate the possibility of crack propagation. For all the analyses, the safety factors obtained exceeded the minimum safety factors generally adopted for this type of equipment, indicating that the vessel is of adequate strength and ultimately safe to be used for the intended purpose.

1.0 Introduction

This report describes in detail the design of a pressure vessel for handling hydrocarbon fluids at pressures up to 200 MPa and temperatures from 253 K up to 473 K. The pressure vessel is used as a component of a vibrating-wire viscometer-densimeter for measuring the viscosity and density of fluids. The vessel is principally a hollow cylinder with a plug and screw cap. The end closure consists of plug to cover the opening of the vessel, the cap to hold on the plug in position against the internal pressure within the vessel and a pressure tight seal (GT Ring 126-21400-731-0450) between the plug and the vessel. The figures below show the three components of the vessel.

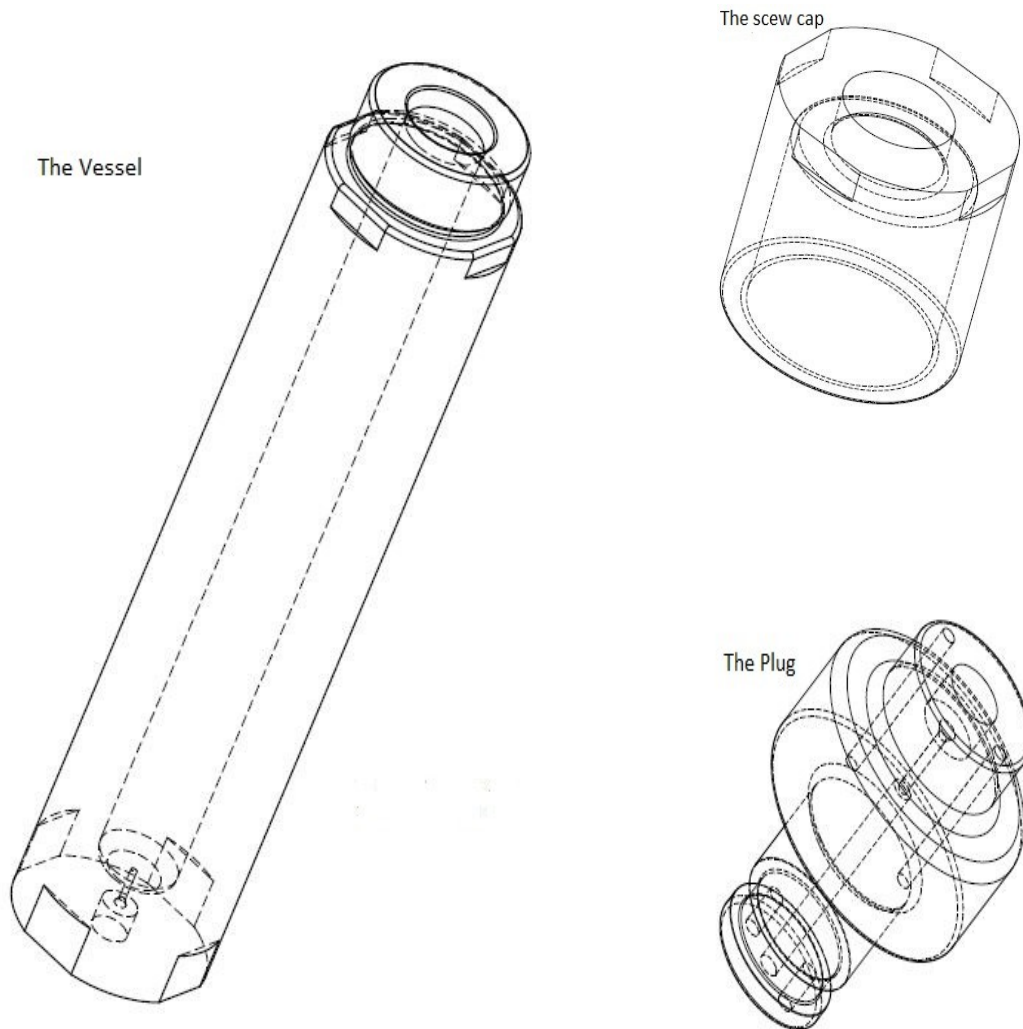


Figure C.1: components of the pressure vessel

The assembly of the three components of the vessel is as shown in the following figure.

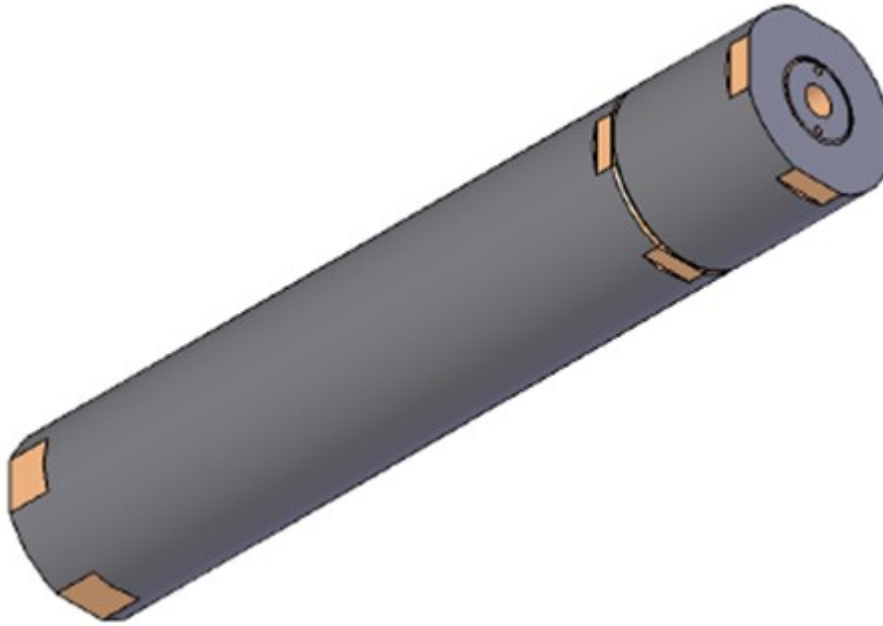


Figure C.2: the Assembly of the vessel components

2.0 The Design

In this document, the design for adequate strength approach was adopted which is fundamentally based on a calculation method. In order to meet the design requirements of 200 MPa and 473 K, a martensitic precipitation hardening Stainless steel (AISI type 17-4 PH, EU designation 1.4542) was chosen as the material of construction. This grade of stainless steel provides an outstanding combination of high strength, good corrosion resistance, favourable mechanical properties at temperatures up to 589 K and good toughness. The barrel was designed to an outer diameter of 79 mm and an inner diameter of 31.75 mm.

3.0 Material Properties

Stainless steel (17-4PH)

The steel was purchased from *AK steel Ltd* as a condition A round stainless steel bar with the suppliers' invoice number 0000010496. The purchase was accompanied with the material certificate which detailed the mechanical properties (yield and ultimate tensile strength) of the metal both in conditions A (as supplied) and for condition H 900 at room temperature as given in Table C.1. These data were obtained by measurements on the actual lot from which the billet was cut, as cross-referenced by the heat number given on the suppliers invoice.

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Table C.1: Mechanical properties of (17-4PH) Condition A and H 900 at room temperature

MATERIAL PROPERTIES		Cond. A	H 900
Material data from the supplier	σ_u /MPa	1118	1373
	σ_y /MPa	821	1282
	Hardness = 45 Rockwell C for H 900		

After machining, the three components of the vessel were heat treated to condition H900 and the heat-treatment company determined that the required hardness stipulated in table (1.0) was achieved.

Since the vessel is intended for application at maximum service temperature up to 473.15 K, it is necessary to perform the design calculations based on the mechanical properties at the maximum service temperature. Mechanical properties (tensile and yield strength) of 17-4PH both at ambient and higher temperatures were given by Bohler^[9] and comparisons between the properties (at ambient temperature) of the metal used in this design closely matched the values given by Bohler shown in Figure C.3 below.

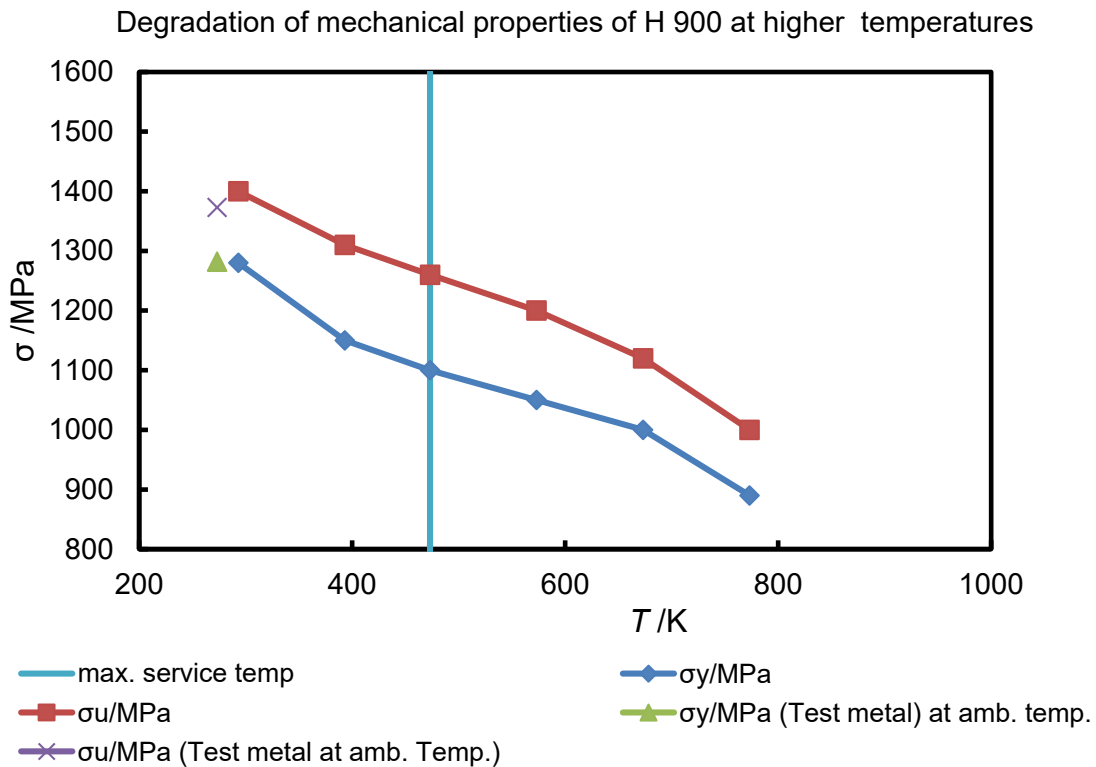


Figure C.3: Degradation of mechanical properties of 17-4PH (Condition H 900) [9]

So, in order to evaluate the properties of the metal at the intended maximum service temperature 473.15K, ratios of the properties at ambient temperature to the maximum

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service temperature (from Bohler) were applied to the ambient properties Table C.1 above and the resulting properties at the maximum service temperature were obtained for the metal actually used as shown in Table C.2 below.

Table C.2: mechanical properties of the metal at ambient and maximum service temperatures

MATERIAL PROPERTIES		293.15 K	473.15 K
Metal used 17-4PH (H 900)	σ_y /MPa	1282	1140
	σ_u /MPa	1373	1274
	T_{max} /MPa	641	570

3.1 Vessel dimensions

The vessel was designed to the dimensions shown in Table C.3 below.

Table C.3: Dimensions of the vessel

17-4PH (H 900)	Vessel dimensions	Internal, i	Outside, o
	d /mm	31.75	79.00
	r /mm	15.86	39.50
	h /mm	327.50	353.00
	t_w /mm	23.63	
	t_b /mm	25.5	
	V /L	0.26	
	V_{net} /L	0.12	

3.2 Pressure specifications:

Maximum working pressure, $p_{w, max}$ = 200 MPa

Design pressure p_d = $1.1 p_{max,w} = 220$ MPa

Test pressure, p_{test} = $1.2 p_{max,w} \frac{p_b(T_{test})}{p_b(T_{max})} = 263$ MPa

4.0 Calculation for the Main Bore

4.1 Bursting pressure

For monobloc vessels, of known origin but free from cross-bores and welding, for use under creep-free and fatigue-free conditions, the bursting pressure is given by^[10]:

$$p_b = 2\sigma_u \left(\frac{K-1}{K+1} \right) \quad (4.0)$$

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where, p_b is the bursting pressure of the vessel in MPa, σ_u is the ultimate tensile strength MPa, and K is the diameter ratio, defined by

$$K = \frac{d_o}{d_i} \quad (4.1)$$

By using equation (4.0) above, the bursting pressures at both the ambient and maximum service temperatures are calculated and the results tabulated as shown in table 1.3.

4.2 Yield pressure

The yield pressure is calculated from the diameter ratio and the yield strength of the material using equation (4.2) shown below:

$$p_y = \frac{\sigma_y}{2} \left(\frac{K^2 - 1}{K^2} \right) \quad (4.2)$$

The yield pressures at ambient and maximum service temperatures are shown in Table C.4 below.

Table C.4: Burst and yield pressures at ambient and maximum service temperatures

Burst and yield pressures		$T = 293.15$ K	$T = 473.15$ K
17-4PH (H 900)	p_b/MPa	840	766
	p_y/MPa	456	405

Since, the yield pressure (at test condition) is higher than the test pressure, autofretting of the bore will not occur during pressure testing.

4.3 Safety factors

A minimum safety factor N of 1.3 for the stress conditions experienced under the test pressure against the maximum allowable stress, is generally adopted for high pressure equipment design. The safety factors on the test pressure for both the burst and the yield pressures are calculated using the following equations.

For burst pressure,

$$N = \frac{p_b}{p_{\text{test}}}, \quad (4.3)$$

and, the safety factor on yield pressure is

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$$N = \frac{p_y}{p_{test}} \quad (4.4)$$

The safety factors are tabulated as shown in Table C.5 below.

Table C.5: Safety factors for burst and yield pressure

Burst and yield pressures		T = 293.15 K	T = 473.15 K
17-4PH (H 900)	N_b	3.2	2.9
	N_y	1.7	1.5

The safety factors are greater than the minimum value of 1.3 highlighted above

4.4 Maximum shear stress criterion

For a thick wall vessel with closed ends subjected to internal pressure p_i and zero external pressure, the maximum stress occurs at the inner bore of the vessel and the three principal stresses σ_1 , σ_2 and σ_3 , corresponding to the geometrical (cylindrical) stresses σ_t , σ_r and σ_i can be evaluated as a functions of radius using *Lame's equations* given below.

The tangential stress σ_t at any given radius r between $r_i \leq r \leq r_o$ is giving by:

$$\sigma_t = \frac{p_i r_i^2 - p_o r_o^2 - r_i^2 r_o^2 (p_o - p_i) / r^2}{r_o^2 - r_i^2} \quad (4.5)$$

Similarly, the radial stress σ_r at any given radius r , between $r_i \leq r \leq r_o$ is:

$$\sigma_r = \frac{p_i r_i^2 - p_o r_o^2 + r_i^2 r_o^2 (p_o - p_i) / r^2}{r_o^2 - r_i^2} \quad (4.6)$$

Since the vessel has a closed ends, it is subject to a longitudinal stress given by:

$$\sigma_i = \frac{p_i r_i^2 - p_o r_o^2}{r_o^2 - r_i^2} \quad (4.7)$$

The principal stresses as well as the maximum shear stress were calculated at inner bore of the vessel using the above equations and the results are shown in Table C.6 below.

Table C.6: Principal stresses at both the inner bore and the outside of the vessel

17-4PH (H 900)	Principal stresses	Inner bore	Outside dia
	σ_t / MPa	363	163
	σ_r / MPa	-200	0
	σ_i / MPa	81	81

	$T_{\max}$ /Mpa	281	81
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5.0 Calculation for Blind Bottom of the Vessel

5.1 Determining the blind end closure thickness

The minimum thickness t_b of the blind end closure was determined according to the method of Dixon and Perez^[11] which, for cylindrical wall ratio K between 1.5 and 2.25, gives:

$$t_b = t_w(-1.06667K^3 + 6.80K^2 - 15.433K + 13.45) \quad (5.0)$$

where, t_w is the minimum wall thickness according to ASME design code, section VIII division 3 given by:

$$t_w = \frac{D_i(K-1)}{2} \quad (5.1)$$

and, the wall ratio K :

$$K = \exp(p_d / S) \quad (5.2)$$

For high strength materials,

$$S = \frac{\sigma_y}{3} \quad (5.3)$$

$$K = \exp\left(\frac{3p_{\max,w}}{\sigma_y}\right) \quad (5.4)$$

The results from the equations above were summarised in the table below.

Table C.7: Calculations for the blind end closure thickness

Blind end closure thickness		calculated	designed
17-4PH (H 900)	t_w / mm	10.69	13.66
	t_b / mm	22.81	25.50
	K	1.67	1.86

Summary and Conclusions

	P_d /MPa	220
	σ_y /MPa	1282
	D_i /mm	31.75
	S / MPa	427.33

5.3 Effect of stress concentration due to fillet radius at the bottom of the vessel

The maximum stress intensity at the fillet corner radius can be calculated by the following formula ^[11].

$$S_i = K_c \left[\frac{(K^2 + 1)}{(K^2 - 1)} \right] p_d \quad (5.5)$$

S_i is the stress intensity at the fillet

Y is the wall thickness ratio given by equations (1.10) and (1.12)

K_c is the stress concentration factor applied to the bore hoop stress in the cylindrical shell and is given by ^[11] equation (1.17) below (for $Rc = 0.35t_w$)

$$K_c = -0.224K^3 + 1.472K^2 - 3.306K + 4.3924 \quad (5.6)$$

Safety factor

$$N_\sigma = \frac{\sigma_y}{S_i} \quad (5.7)$$

The results of the above calculations were tabulated in the Table C.8 below.

Table C.8: calculations for the effect of stress concentration due to the fillet radius

Stress concentration at fillet radius		
17-4PH (H 900)	p_d /MPa	220
	K	1.67
	K_c	1.932
	S_i /MPa	898
	σ_y /MPa	1282
	N_σ	1.4

6.0 Calculations for the threaded portion

6.1 Tensile stress in the neck

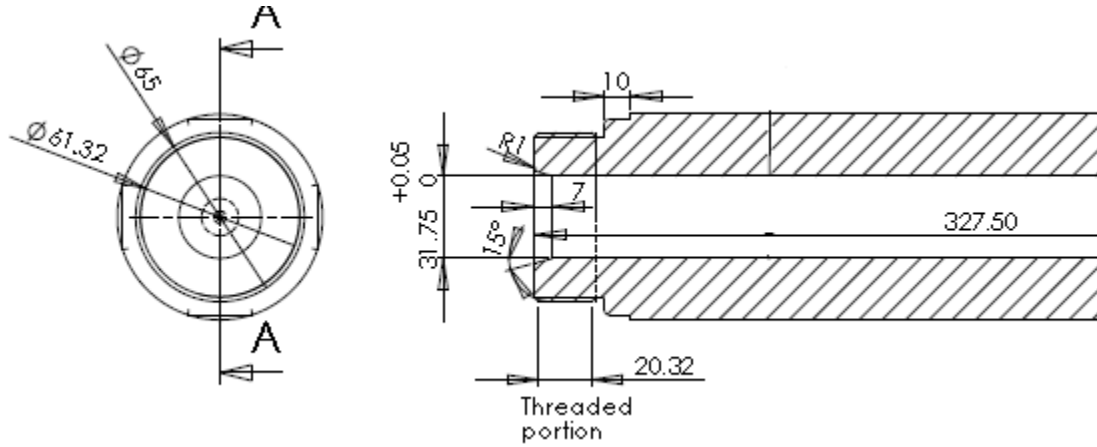


Figure C.4: threaded portion of the vessel

$$\sigma = \frac{F}{A_T} \quad (6.1)$$

where, F is the maximum pressure force at test pressure given by:

$$F = p_{\text{test}} A \quad (6.2)$$

$$A = \frac{\pi d_i^2}{4} \quad (6.3)$$

$$A_t = \frac{\pi(d_t^2 - d_i^2)}{4} \quad (6.4)$$

d_t and A_t are the external diameter and the area of the threaded portion respectively. The table below summarises the calculation for the threaded portion.

Table C.9: Summary of the calculations for the threaded portion

Threaded portion calculations		
17-4PH (H 900)	p_{test} /MPa	263
	A /mm ²	791.73
	F /N	208400
	d_t /mm	55.38
	d_i /mm	31.75
	A_t /mm ²	1617.04
	σ /MPa	129
	N_σ	9.94

7.0 End Closure

The end closure consists of plug to cover the opening of the vessel, the cap to hold on the plug in position against the internal pressure within the vessel and a pressure tight seal (GT Ring 126-21400-731-0450) between the plug and the vessel. Figure C.5 shows a section through the end closure of the vessel.

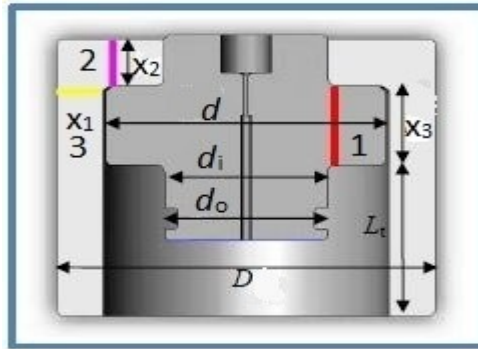


Figure C.5: Section through the end closure of the vessel

where,

D = cap outside diameter

d = cap internal diameter above the thread

d_o = hub internal diameter (plug) = effective sealing diameter

x_1 = cap thickness

x_2 = cap flange thickness

x_3 = hub thickness (plug)

p = internal pressure

A = area based on the d_o

L_t = length of the engaged thread

In Figure C.5 the red colour portions show the circumferential areas under shear stress τ , whereas the yellow regions indicate annular areas subjected to tensile stress σ due to the internal pressure force.

Using stress analysis, the various dimensions can be calculated as follows.

p = maximum pressure within the vessel = p_{test}

also, the area A based on the effective sealing diameter ($d_o = d_i$)

$$A = \frac{\pi d_i^2}{4} \quad (7.0)$$

and the maximum force due to the internal pressure $f_{\max}$ can be evaluated.

$$f_{\max} = P_{\text{test}} A \quad (7.1)$$

Similarly, the tensile stress is obtained from the following equation.

$$\sigma_{\max} = \frac{4f_{\max}}{\pi(D^2 - d^2)} = \frac{2}{3} \sigma_y \quad (7.2)$$

Therefore D is obtained from the above relation.

The threaded part of the vessel where the cap is screwed onto was given a diameter of 65 mm with a thread depth $h = 1.84$ mm, then x_1 can be obtained from the following.

$$x_1 = \frac{D - d}{2} \quad (7.2)$$

where, $d = 65 - 2h$

In a similar manner, x_2 and x_3 were obtained from shear stress criterion as follows.

$$\tau_{\max} = \frac{f_{\max}}{\pi d x_2} = \frac{\sigma_y}{2N} \quad (7.4)$$

also,

$$\tau_{\max} = \frac{f_{\max}}{\pi d_o x_3} = \frac{\sigma_y}{2N} \quad (7.5)$$

Where, N is the safety factor ($N = 4$, and $d_o = 36$ mm [designed])

The minimum length of the engage thread L_t was from the following relation [10].

$$P_{\text{test}} = \frac{D_{\text{mean}} L_t}{2 d_s^2} \sigma_y \quad (7.6)$$

where d_s is the effective diameter of the pressure seal (i.e. internal diameter of the vessel = 31.75 mm)

$$D_{\text{mean}} = d + h \quad (7.7)$$

Therefore, the minimum length L_t is given by;

$$L_t = \frac{2 d_s^2 P_{\text{test}}}{(d + h) \sigma_y} \quad (7.8)$$

Summary and Conclusions

Table C.10 below gives the summary of the calculated minimum dimensions and the designed values

Table C.10: Dimension of the end closure

dimensions		calculated	designed
17-4PH (H 900)	$x_1/ \text{ mm}$	1.24	8.8
	$x_2/ \text{ mm}$	6.75	16
	$x_3/ \text{ mm}$	11.50	28
	$L_t / \text{ mm}$	6.55	20.32
	$A / \text{ mm}^2$	791.73	
	$f_{\max} / \text{ N}$	208400	
	$\sigma_{\max} / \text{ MPa}$	855	
	$\tau_{\max} / \text{ MPa}$	160	
	$D / \text{ mm}$	63.80	
	$d / \text{ mm}$	61.32	
	$d_{o,t} / \text{ mm}$	36.00	
	$h / \text{ mm}$	1.84	
	N_r	4	

8.0 Calculation for the Plug Closure

8.1 Shear stress on the flange

The shear stress in region (1-1) shown in Figure C.5 can be determined from the following equation.

$$f_{\max} = P_{\text{test}} A \quad (8.0)$$

$$A = \frac{\pi d_i^2}{4} \quad (8.1)$$

$$\tau = \frac{f_{\max}}{A_f} \quad (8.2)$$

Where, A_f is the area of the flange given by

$$A_f = \pi d_i x_3 \quad (8.3)$$

8.2 Effect of stress concentration at the neck of the plug due to fillet radius

The ratios

$$\frac{d}{d_i} = 1.93$$

and,

$$\frac{r}{d_i} = 0.063$$

Where, r is the fillet radius, d is the diameter of the wider section and d_i is the diameter of the narrow section

From figure 72 (pp 96) of reference^[12] the stress concentration factor for a stepped round bar with a shoulder fillet having the ratios $d/d_i = 1.93$ and $r/d_i = 0.063$ is given as $K_c = 2.26$.

Therefore the actual stress below and above the flange of the plug is given by:

$$\tau_{\text{actual}} = K_c \tau_o \quad (8.4)$$

where , K_c is the theoretical stress-concentration factor and τ_o is the nominal shear stress.

The safety factor is given by:

$$N_\tau = \frac{\tau_{\text{max}}}{\tau} \quad (8.5)$$

The table below gives the values calculated for the shear stress and the safety factor based on the above equations.

Summary and Conclusions

Table C.11: Calculations for the plug

Calculations for the plug		
17-4PH (H 900)	$p_{\text{test}} / \text{MPa}$	263
	A / mm^2	791.73
	F / N	208400
	d / mm	61.32
	x_3 / mm	11.50
	A_f / mm^2	1146.90
	τ / MPa	182
	K_c	2.26
	$T_{\text{actual}} / \text{MPa}$	411
	$\tau_{\text{max}} / \text{MPa}$	551
	N_r	3.0
	$N_{r_{\text{act}}}$	1.3

9.0 Calculations for the Screw Cap

9.1 Cap shear stress

The shear stress around region (2-2) in Figure C.5 above can be calculated using the following relations.

$$f_{\text{max}} = p_{\text{test}} A \quad (9.0)$$

$$A = \frac{\pi d_i^2}{4} \quad (9.1)$$

$$\tau = \frac{f_{\text{max}}}{A_c} \quad (9.2)$$

where,

$$A_c = \pi d x_2 \quad (9.3)$$

9.2 Tensile stress in the threaded portion of the cap

The tensile stress around region (3-3) of the cap can be obtained from the following equations.

$$f_{\text{max}} = p_{\text{test}} A \quad (9.4)$$

$$A = \frac{\pi d_i^2}{4} \quad (9.5)$$

$$\sigma = \frac{f_{\max}}{A_t} \quad (9.6)$$

where, A_t is the annular area above the threaded portion of the cap given by:

$$A_t = \frac{\pi}{4} (D^2 - d^2) \quad (9.7)$$

Effect of stress concentration at the neck of the cap due to shouldered fillet radius

From chart 3.4 of reference ^[13], stress concentration factor for a shouldered fillet is given by:

$$K_c = C_1 + C_2 \left(\frac{2e}{d_o} \right) + C_3 \left(\frac{2e}{d_o} \right)^2 + C_4 \left(\frac{2e}{d_o} \right)^3 \quad (9.8)$$

where:

K_c = stress concentration factor

d_o = outside diameter of the cap

d_i = inside diameter of the cap

e = wall thickness of the cap

r = fillet radius

Calculating the ratio:

$$\frac{e}{r} = 3.375$$

For $2.0 \leq e/r \leq 20.0$,

$$C_1 = 1.200 + 0.860\sqrt{e/r} - 0.022e/r \quad (9.9)$$

$$C_2 = -1.805 - 0.346\sqrt{e/r} - 0.038e/r \quad (9.10)$$

$$C_3 = 2.198 - 0.486\sqrt{e/r} + 0.165e/r \quad (9.11)$$

$$C_4 = -0.593 - 0.028\sqrt{e/r} - 0.106e/r \quad (9.12)$$

Therefore, the actual stresses due to effect of stress concentration at the shouldered fillet are:

$$\sigma_{\text{actual}} = \sigma K_c \quad (9.13)$$

$$\tau_{\text{actual}} = K_c \tau_o \quad (9.14)$$

Summary and Conclusions

where , K_c is the theoretical stress-concentration factor

τ_o is the nominal shear stress

The safety factor on the yield strength is given by:

$$N_\sigma = \frac{\sigma_y}{\sigma} \quad (9.15)$$

The table below gives the values calculated for both shear and tensile stresses and their safety factors based on test pressure.

Table C.12: Calculations for screw cap

Calculations for the screw cap		
17-4PH (H 900)	A / mm^2	791.73
	F / N	208400
	D / mm	63.80
	d / mm	61.32
	x_2 / mm	6.75
	A_t / mm^2	243.83
	A_c / mm^2	1300.43
	K_c	0.97
	τ / MPa	160
	$\tau_{\text{actual}} / \text{MPa}$	155
	$\tau_{\text{max}} / \text{MPa}$	641
	σ / MPa	855
	$\sigma_{\text{actual}} / \text{MPa}$	825
	σ_y / MPa	1282
	N_r	3.6
	N_{Tactual}	4.1
	N_σ	1.5
	$N\sigma_{\text{actual}}$	1.6

Conclusions

The design of 200 MPa pressure vessel has been reported and detail calculations and analysis were presented. Stress analysis at different parts of the vessel including the critical (weakest) parts demonstrated safety factors higher than the minimum safety factors generally considered for this type of high pressure equipment, therefore, the vessel is considered safe and of adequate strength for the intended purpose.

Summary and Conclusions

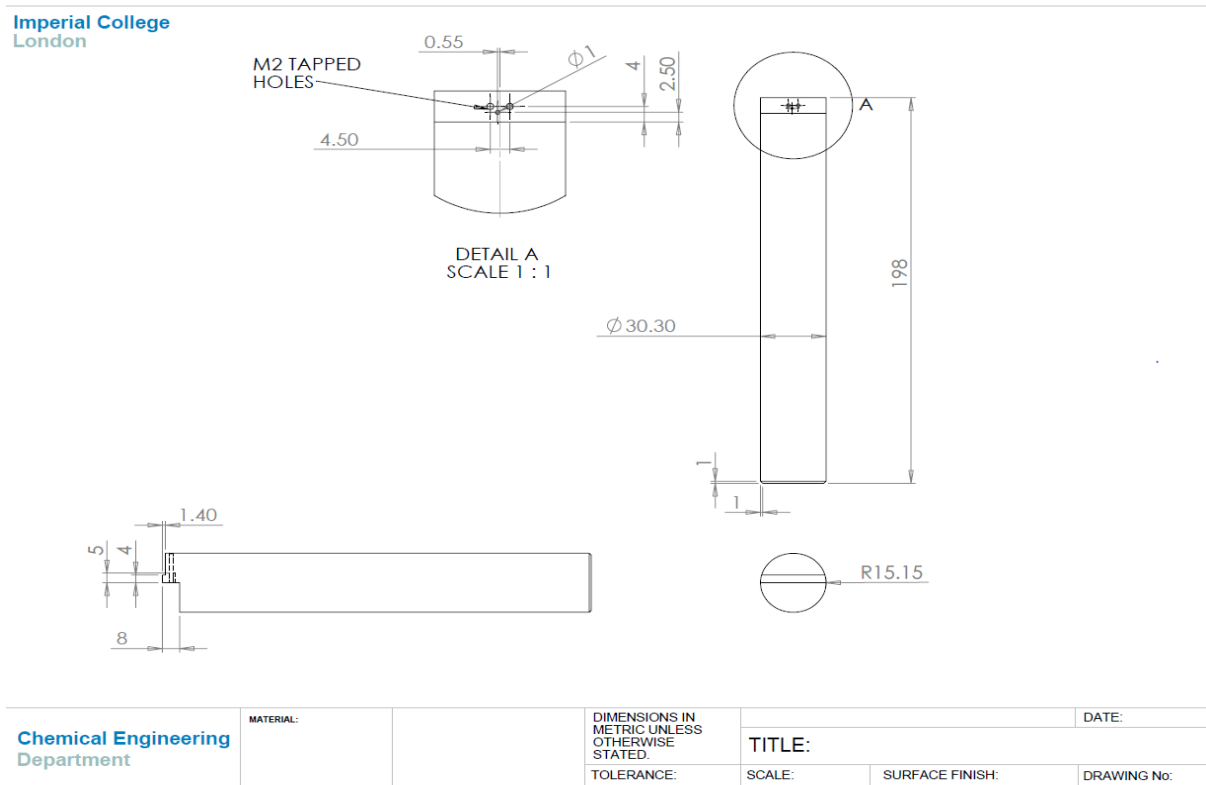


Figure C.6: The Engineering drawing of the new Aluminium Sink

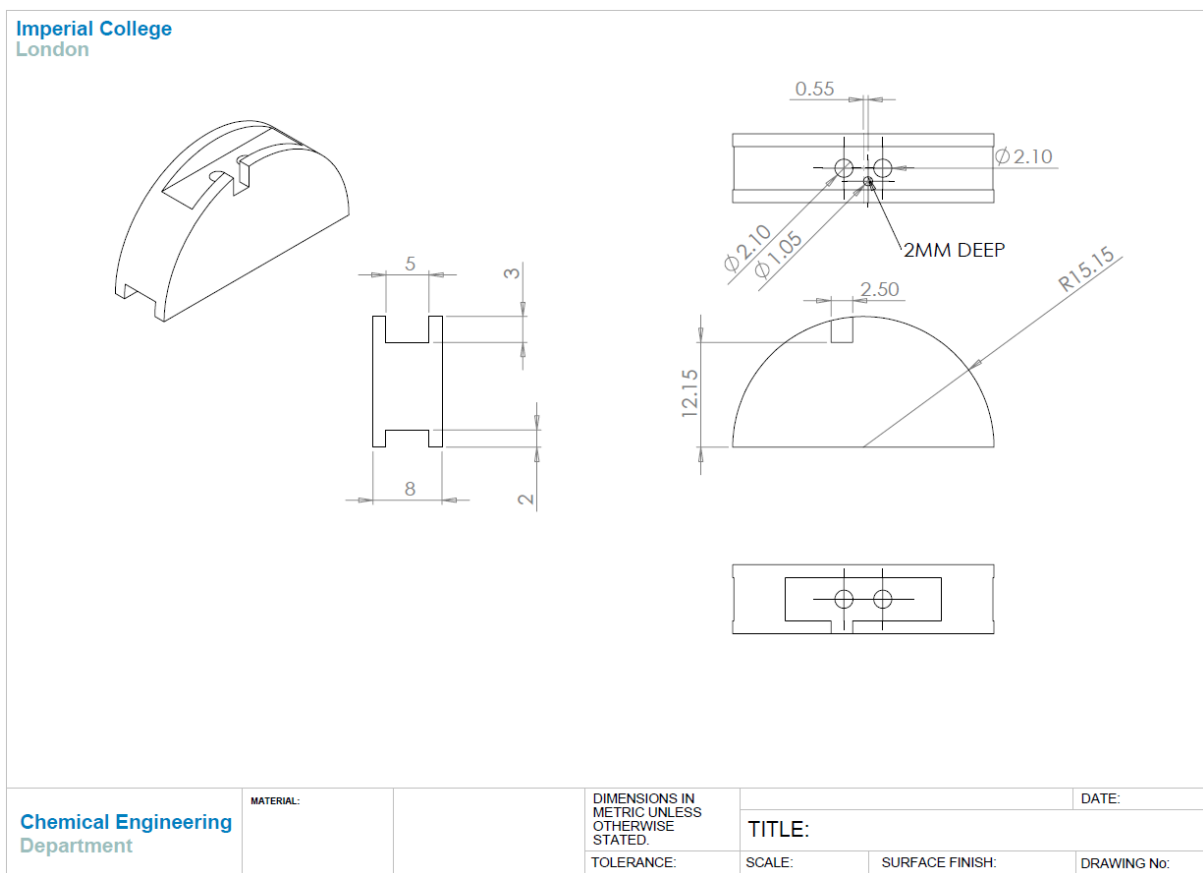


Figure C.7: The Engineering drawing of the new Aluminium clamp

Appendix D: Standard Operating Procedure

Introduction

The standard operating procedure (SOP) presented in this document will provide a step-by-step instructions for the optimum and safe operation of the vibrating-wire viscometer-densimeter (VWVD). The system comprises four modules namely: the fluid handling system, the accumulator, the vibrating-wire cell and the gas booster (Model S-86-JN-60) for preparing mixtures at high pressures as shown in Figure 5.1 in chapter 5. The sequence of activities to be followed to carry-out simultaneous viscosity and density measurements on both pure liquid components and mixtures using the VWVD is described in the following sequence of operations and illustrated in Figures D1 and D2.

PREPARING THE '500 ml WEIGHING CYLINDER

- Examine the 500 mL weighing cylinder making sure that is clean and corrosion-free from the inside. Carry out a leak test to ensure that the connections are gas-tight.

PREPARING THE GAS BOOSTER

- Examine the gas booster to ensure that all the connections are gas-tight.

FILLING THE '500 mL WEIGHING CYLINDER' USING THE GAS BOOSTER

- Connect the drive air supply to the 'air-in valve' on the booster
- Connect the test gas supply to the 'gas-in valve' on the booster
- Set the supply pressure of the test gas to not more than 10 MPa
- Connect the weighing cylinder to the 'gas out' port of the booster
- Open the drive air valve to start the booster
- Open both 'gas-in' and 'gas-out' valves on the booster
- Monitor the outlet pressure from the pressure sensor on the booster and also check for leaks during the filling operation
- Close the valve on the weighing cylinder and stop the booster by shutting both the 'air-in' and the 'gas-in' valves on the booster and also the test gas supply regulator on the cylinder
- In the event that a leak is detected during filling, shutdown the booster, close all valves and remove the weighing cylinder to a fume cupboard

SYSTEM CLEANING

STEP I: Blowing with nitrogen gas at low pressure (e.g. 0.3 MPa)

- With valves V_4 , V_5 , V_6 , V_7 , V_8 and V_9 open, inject nitrogen gas to the system through the gas valve, V_3 to expel the existing fluid in the system including the accumulator
- Collect the fluid via the drain valve V_4
- Close valves V_3 and V_4

STEP II: Flushing with a volatile solvent

- Create a rough vacuum in the system by pumping through valve V_2
- With valves V_5 , V_6 , V_7 , V_8 and V_9 still open, fill the system with a suitable volatile solvent (e.g. hexane) through valve V_1
- Run the circulation pump to circulate the solvent around the system
- Raise the solvent bottle above the apparatus and allow solvent to pass through the system and to the waste bottle via V_4
- Collect fluid via the drain valve V_4
- Repeat step I above to get rid of the residual solvent in the system

EVACUATION AND DRYING

STEP I: Evacuating the system using vacuum pump

Summary and Conclusions

- Open valves V_5 , V_6 , V_7 , V_8 , V_9 and V_2 to ensure complete evacuation of the system including the accumulator
- Raise the temperature of both the liquid handling system and the accumulator to about 313 K
- Raise the temperature of the vibrating-wire cell and the piping ideally to above the boiling point of the solvent used in step II
- Maintain the system under vacuum for a few hours. During this time, additional N_2 flushing operation may also be carried out.

SAMPLE PREPARATION AND SYSTEM FILLING

- Place liquid sample in a solvent bottle and degas under vacuum
- Connect the solvent bottle to the valve box via inlet valve V_1
- Isolate the accumulator by closing valves V_7 and V_8 on the accumulator enclosure
- Close the vacuum pump valve V_2 and open the inlet valve V_1 to draw in liquid from the solvent bottle

SINGLE COMPONENT FLUID AND LIQUID MIXTURES

- Use the manual syringe pump to draw-in more liquid to fill the system to the point at which pressure can be raised
- Set the desired operating temperature
- When the temperature is stable adjust the pressure to the desired value and make measurements
- Multiple strokes of the syringe pump may be used to raise the pressure to a maximum of 200 MPa

MIXTURE OF LIQUID WITH DISSOLVED GAS

STEP I: Preparing mixtures in-situ

- Weigh the bottle containing the liquid sample
- Isolate the accumulator by closing valves V_7 and V_8
- Introduce liquid sample to the system via the inlet valve V_1
- Inject more liquid to raise pressure and if desired make measurements at high pressures up to 200 MPa
- Disconnect and drain the liquid in the PTFE tube back to the solvent bottle
- Re-weigh the bottle to determine the actual mass of liquid transferred
- Lower pressure as much as possible by using the injector
- Lower pressure further by slowly opening valve V_7 to bleed liquid into the accumulator until V_7 is fully open
- Carefully fill the weighing cylinder with the gas to a sufficient pressure (not greater than 35 MPa) using the gas booster shown in the figure above
- Weigh the weighing cylinder before transferring gas to the system
- With the inlet valve V_1 closed connect the weighing cylinder and open the valve at the top of the cylinder to fill the 1/8" tube connecting the weighing cylinder and the valve box
- Close the cylinder valve and then open the inlet valve V_1 to transfer the gas in the line to the system
- Close the inlet valve and disconnect the cylinder and re-weigh it to account for the mass of gas in the 1/8" tube between the weighing cylinder and the valve box. Calculate volume of this tube

Summary and Conclusions

- Connect the cylinder again and open the inlet valve V_1 to transfer some amount of gas from the weighing cylinder to the system and also to push the liquid into the system
- Actuate the circulation pump to enable thorough mixing
- Stop gas filling when the system pressure is approximately equals the desired bubble point pressure of the mixture (which should be lower than the m.w.p of the accumulator $p < 28$ MPa) at the filling temperature
- Disconnect the weighing cylinder and re-weigh it on a balance to determine the mass of the gas transferred to the system
- Back calculate the actual mixture composition from the known masses of liquid and gas injected into the system

STEP II: Homogenising the mixture

- Adjust the temperature of the system, raise the pressure (a bit) and keep mixing to bring the mixture to a single phase
- Continue to actuate the magnetic circulation pump for about 12 hours or so, until homogenisation is achieved
- Periodically open V_9 and close V_8 to flush the accumulator bypass loop

STEP IV: Measurement

- Isolate the accumulator by closing valves V_7 , V_8 and open V_9
- Adjust the pressure and (if necessary) the temperature to the required state point
- When the temperature is stable adjust the pressure to the desired value and make measurements
- Withdraw more fluid from the accumulator to enable measurement at higher pressures (and go to step IV)
- Prepare the next composition by adding an appropriate amount of gas (and go to step IV)
- Repeat the procedure above

SYSTEM DRAINING AND WASTE DISPOSAL

- Depressurise by bleeding some of the mixture back to the accumulator and/or by back stroke of the syringe pump
- Set the temperature controller to a lower value and then accelerate the cooling process by passing compressed air via the heat exchanger surrounding the pressure cell
- Drain liquid/mixture to the drain bottle via valve V_4 ; Flush gas will pass to the vent line
- Flush with compressed air to discharge any residual liquid/mixture
- Dispose-off the liquid/mixture in the appropriate waste container
- Shut down by switching-off temperature control and allowing system to cool to a safe temperature

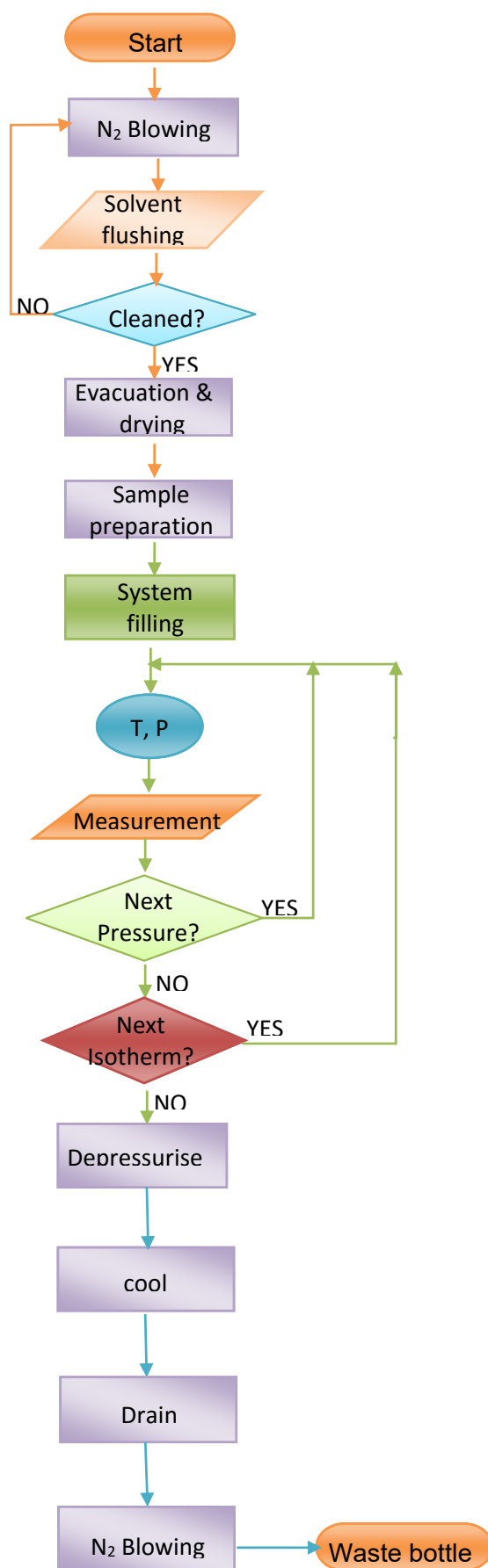


Figure D1: Flow chart for viscosity and density measurements for single liquid component

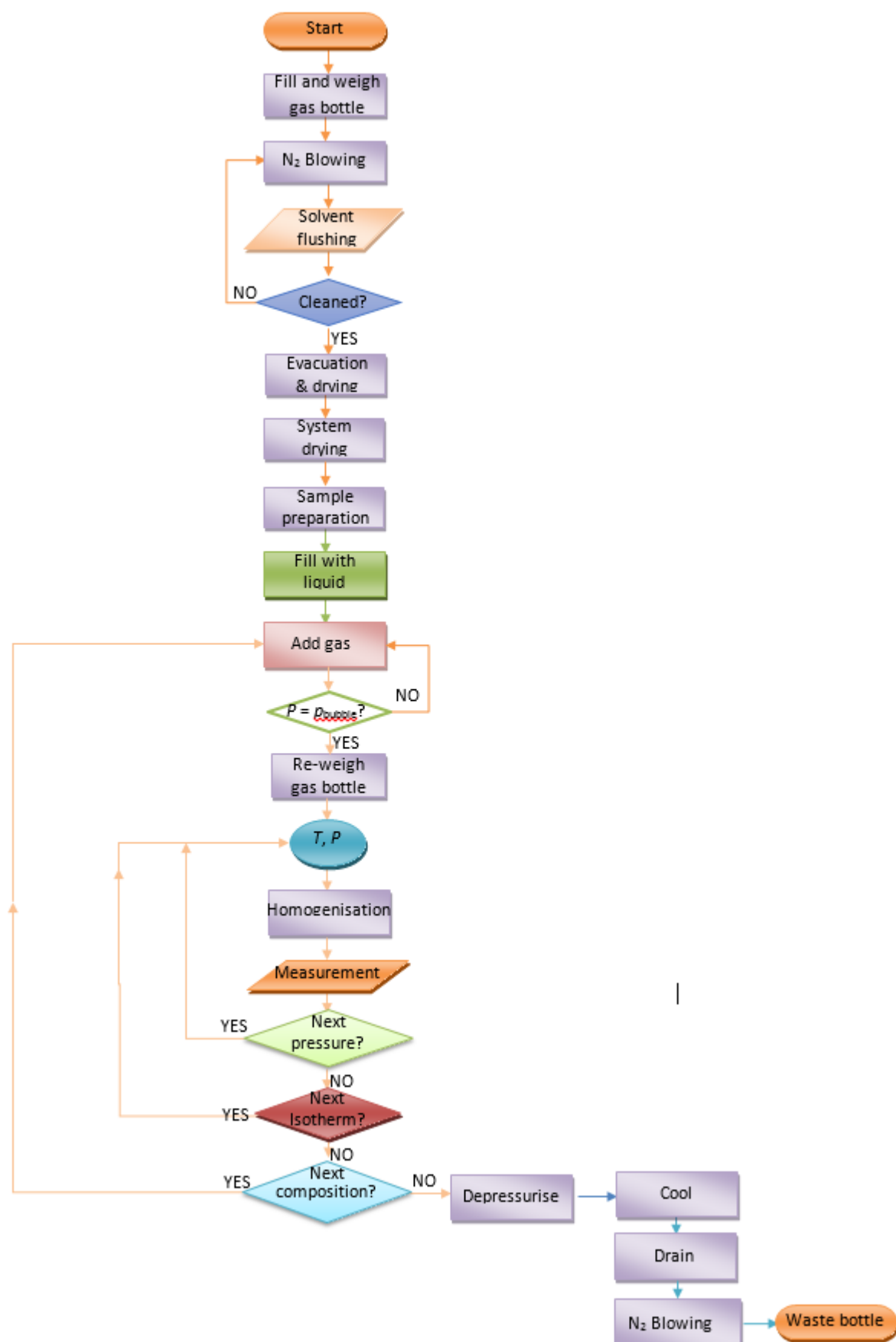


Figure D2: Flow chart for viscosity and density measurements for mixtures of liquid with dissolved gas

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