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Department of Earth Science and Engineering

Centre for Petroleum Studies

The Influence of Aromatic Compounds on Viscosity

By

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**A report submitted in partial fulfilment of the requirements for
the MSc and/or the DIC.**

September 2014

Declaration of Own Work

I declare that this thesis

The Influence of Aromatic Compounds on Viscosity

is entirely my own work and that where any material could be construed as the work of others, it is fully cited and referenced, and/or with appropriate acknowledgement given.

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Abstract

Reservoir fluids are complex mixtures of hydrocarbons containing paraffins, naphtenes and aromatic compounds. Theoretical models have been developed to quantitatively represent hydrocarbon mixture viscosity. This paper enhances the ability of the Vesovic-Wakeham (VW) method to predict the viscosity of aromatic mixtures and hence its ability to model the viscosity of petroleum fluids.

The VW method has been applied to predict the viscosity of aromatic mixtures of benzene and alkane. Binary mixtures of benzene + *n*-hexane (*n*-C₆), *n*-octane (*n*-C₈), *n*-decane (*n*-C₁₀), *n*-dodecane (*n*-C₁₂) or *n*-hexadecane (*n*-C₁₆) are assessed at 298 K and 1 bar. The effect of density on the pure species parameter was studied and the effect of the reference correlation on the mixture viscosity prediction. The VW method predicted viscosity mixtures of benzene and *n*-C₆ within the experimental uncertainty, with maximum deviation of 3.9%. For mixtures with heavier alkanes a greater MD of up to 20% was obtained. As the alkane critical density exceeded that of benzene, extrapolation of the reference correlations was required into the 2-phase region.

A new reference correlation for benzene has been added to the VW framework and a new reference viscosity correlation for *p*-xylene has been developed. The *p*-xylene viscosity correlation proposed is based upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory. It is applicable in the temperature range from (288 to 673) K at pressures up to 1100 bar with maximum deviation (MD) of 2.7%.

Table of Contents

Declaration of Own Work	i
Acknowledgements	ii
List of Figures.....	v
List of Tables.....	vi
Abstract.....	1
Introduction	1
DEVELOPING A CORRELATION FOR THE VISCOSITY OF <i>p</i> -XYLENE.....	2
Experimental Viscosity Data.....	2
Methodology and Analysis.....	3
Overall Viscosity Correlation.....	9
Computer-Program Verification.....	10
MODELLING THE VISCOSITY OF AROMATIC-ALKANE BINARY MIXTURES.....	10
Theory and Methodology	10
Experimental Data.....	11
Results and Discussion.....	12
Conclusion and Recommendation	14
Nomenclature	14
References	15
Appendix	17
Appendix A – Critical Literature Review	17
Appendix B – Miscellaneous Results for the Empirical Correlation for <i>p</i> -Xylene	26
Appendix C – Miscellaneous Results for VW Method for Mixtures	27

List of Figures

Figure 1 – Distribution of the available experimental viscosity data of <i>p</i> -xylene	3
Figure 2 – Percentage deviations $[100(\eta_{corr} - \eta_{exp})\eta_{exp}]$ from the experimental data of Vogel and Hendl (1992) in the limit of zero-density	4
Figure 3 – Percentage deviations $[100(\eta_{corr} - \eta_{exp})\eta_{exp}]$ of the available experimental data in the vapour phase at pressures below 2 bar	5
Figure 4 – Percentage deviations $[100(\eta_{exp} - \eta_{fit})\eta_{exp}]$ of the primary experimental viscosity data at 323 K and 348 K from the quadratic fit in density to Kashiwagi and Makita (1982) data	6
Figure 5 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})\eta_{exp}]$ of primary experimental viscosity data in the liquid region	7
Figure 6 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})\eta_{exp}]$ of the primary experimental viscosity data at 323 K and 348 K in the liquid region	8
Figure 7 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})\eta_{exp}]$ of primary experimental viscosity data measured at 1 bar	8
Figure 8 – Viscosity of <i>p</i> -xylene as a function of density along isotherms	9
Figure 9 – Percentage deviations $[100(\eta_{exp} - \eta_{VW})\eta_{exp}]$ of different pure species conditions on the VW method predictive capabilities for the mixture of benzene with <i>n</i> -C ₆ of Lal <i>et al.</i> (2000)	12
Figure 10 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with <i>n</i> -C ₆	13
Figure 11 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with <i>n</i> -C ₈	13
Figure 12 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with <i>n</i> -C ₁₀	13
Figure 13 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with <i>n</i> -C ₁₂	13
Figure 14 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with <i>n</i> -C ₁₆	13
Figure C1 – Percentage deviation $[100(\eta_{exp} - \eta_{VW})\eta_{exp}]$ between experimental viscosity of Lal <i>et al.</i> (2000) and calculated viscosity using VW method for different mixing rules for χ_{ij} for a mixture of benzene with <i>n</i> -C ₆	27
Figure C2 – Percentage deviation $[100(\eta_{exp} - \eta_{VW})\eta_{exp}]$ between experimental viscosity of Awwad <i>et al.</i> (1986) and calculated viscosity using VW method for different mixing rules for χ_{ij} for a mixture of benzene with <i>n</i> -C ₁₂	27
Figure C3 – Percentage deviations $[100(\eta_{exp} - \eta_{VW})\eta_{exp}]$ of different pure species conditions on the VW method predictive capabilities for the mixture of benzene with <i>n</i> -C ₁₂ of Awwad <i>et al.</i> (1986)	28

List of Tables

Table 1 – Primary Data Used In Developing the Viscosity Correlation of <i>p</i> -Xylene	2
Table 2 – Coefficients for the Empirical Fitting of the Zero-Density Limit Viscosity, Eq.(4)	4
Table 3 – Coefficients for the Empirical Fitting of the Initial Density Dependence, Eq.(6).....	5
Table 4 – Coefficients for the Representation of the Residual Viscosity, Eq. (7).....	7
Table 5 – Evaluation of the <i>p</i> -Xylene Viscosity Correlation against the Primary Experimental Data.....	9
Table 6 – Sample Points for Computer Verification of the Correlation Equations	10
Table 7 – Experimental Data for Mixture Viscosities	11
Table A1 – Milestones in Prediction of Viscosity of Dense Mixtures	17
Table B1 – Data Used In Developing the Viscosity Correlation of <i>p</i> -Xylene	26

The Influence of Aromatic Compounds on Viscosity

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Abstract

Reservoir fluids are complex mixtures of hydrocarbons containing paraffins, naphthenes and aromatic compounds. Theoretical models have been developed to quantitatively represent hydrocarbon mixture viscosity. This paper enhances the ability of the Vesovic-Wakeham (VW) method to predict the viscosity of aromatic mixtures and hence its ability to model the viscosity of petroleum fluids.

The VW method has been applied to predict the viscosity of aromatic mixtures of benzene and alkane. Binary mixtures of benzene + *n*-hexane (*n*-C₆), *n*-octane (*n*-C₈), *n*-decane (*n*-C₁₀), *n*-dodecane (*n*-C₁₂) or *n*-hexadecane (*n*-C₁₆) are assessed at 298 K and 1 bar. The effect of density on the pure species parameter was studied and the effect of the reference correlation on the mixture viscosity prediction. The VW method predicted viscosity mixtures of benzene and *n*-C₆ within the experimental uncertainty, with maximum deviation of 3.9%. For mixtures with heavier alkanes a greater MD of up to 20% was obtained. As the alkane critical density exceeded that of benzene, extrapolation of the reference correlations was required into the 2-phase region.

A new reference correlation for benzene has been added to the VW framework and a new reference viscosity correlation for *p*-xylene has been developed. The *p*-xylene viscosity correlation proposed is based upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory. It is applicable in the temperature range from (288 to 673) K at pressures up to 1100 bar with maximum deviation (MD) of 2.7%.

Introduction

Understanding viscosity behaviour is integral for reliable reservoir modelling. As hydrocarbon fluids experience conditions of elevated pressure and temperature whether subsurface or in surface facilities, viscosity is required over large regions of phase space. Its knowledge is required for prediction of the mobility of oils and reservoir fluids, as well as designs for processing facilities (Baltatu *et al.*, 1999). It was reported by Hernandez *et al.* (2002) that the majority of the predictive methods for the viscosity of oil used in numerical reservoir simulators, produce an error of 10-20% for light oil and an order of magnitude off for heavy oils. This leads to large error in reserve estimations, which stresses the demand for accurate values of viscosity. Especially considering the production of heavy oil and bitumen, where composition and temperature changes can have a drastic effect on viscosity. In relation to pipeline facilities for crude oil transport, Degiorgis *et al.* (2001) established that the present viscosity models incorporated in numerical simulators for pipelines, produce errors in pressure drop up to 10% for light oils and 300% for heavier oils. This further confronts the requirement for precision in oil viscosity predictions.

There are different approaches to predict mixture viscosity which are presently applied in the oil industry. The more commonly used empirical approach, utilises correlating sets of experimental data. This provides easy and quick formulation with the ability to be amendable for tuning, yielding results of accuracy over well-defined ranges, dependent on the experimental data used. However, in regions outside the experimental data range also when composition changes, the correlation can become highly inaccurate.

Another method is to develop a quantitative theoretical description of viscosity. This involves understanding concepts of the molecular dynamics due to the dependence of viscosity on molecular interactions. Consequently, due the complex nature of viscosity, especially in heavy oil containing multiple differentiating components, it is difficult to estimate this property. Although the greater complexity in formulation, there is a greater reliability and robustness in predictions due to their theoretical basis.

Vesovic and Wakeham (1989) introduced the original VW method, known as VW-sphere, which utilised Enskog (1922) rigid sphere theory of dense gases in order to estimate mixture viscosity. The theory also incorporated the works of Tham and Gubbins (1971), Di Pippo *et al.* (1977) and Sandler and Fiszdon (1979) which improved the predictive capacity in comparison to prior models. However, due to the model basis of rigid spheres, the proposed theory was less effective in accurately predicting the viscosity of large linear molecules. This eventually led to the work of de Wijn *et al.* (2008), proposing to model chained molecules as equally sized,

tangentially joined and rigid segmented spheres. The method assumes that the collision dynamics can be approximated by instantaneous collisions of hard (VW-chain) spheres. In later years, de Wijn *et al.* (2012) extended the work into mixtures of chain molecules with encouraging result in binary alkane mixtures, which supported the conclusion that the improved VW-chain model was capable of accurately reproducing the viscosity of real liquid mixtures. For the VW method to be able to predict mixture viscosity, pure species references viscosity correlations are required for each component within the mixture.

With the high demand for accurate and reliable viscosity values of different crudes in industry, it is found that for lighter alkanes reference correlations exist (Vogel *et al.*, 1998 and Huber *et al.*, 2004), for aromatic hydrocarbons this is not the case. Therefore, predictive methods and correlations are required to be developed and tested for aromatic compounds. The objective of this work is to use an established viscosity correlation for benzene (Avgeri *et al.*, 2014) modelled as a sphere, to explore the application of the VW method for binary mixtures of benzene and alkanes, testing the effectiveness of the model in predicting experimental mixture viscosity. The objective of this work is also to add to the current VW method, a viscosity correlation for another aromatic compound, *p*-xylene, valid over a wide range of temperatures and pressures.

DEVELOPING A CORRELATION FOR THE VISCOSITY OF *p*-XYLENE

Experimental Viscosity Data

A summary of the experimental measurements of the viscosity of *p*-xylene reported in literature can be found in Appendix B. Temperature and pressure range, number of data points measured and the experimental technique employed are stated. Measurements were reported in 19 papers providing 444 data points. The majority of researchers (16 papers, 62 data points) measured only the value of the liquid viscosity at atmospheric pressure and around room temperature.

A critical assessment of the experimental data was performed to classify the data as primary and secondary according to the recommendation of IUPAC Subcommittee of Transport Properties (Assael *et al.* 1990). A well-established criterion which involves classifying primary data as data obtained with experimental apparatus, for which viscosity is measured with high precision with a full working equation. Additionally, the purity of the sample and the purification methods description was used to stratify primary data. However, these criteria can limit the range of data representation. Hence, it is necessary to incorporate secondary data that covers a wide range of conditions, given consistency with the more accurate primary data or theory.

Based on these criteria, 11 datasets were considered as primary data. Table 1 gives a summary of the primary data specifying, temperature and pressure ranges, the technique employed to perform the measurements, the authors' claimed uncertainty and purity of the sample.

Table 1 – Primary Data Used In Developing the Viscosity Correlation of *p*-Xylene

Authors	Year Publ.	Technique Employed	Purity (%)	Claimed Uncertainty (%)	No. of Data	Temperature Range (K)	Pressure Range (bar)
Mamedov and Panchenkov	1955	C	99	2	7	293 – 353	1
Mamedov <i>et al.</i>	1968	C	99.78	2	129	323 – 548	1 – 400
Nissema and Koskenniska	1972	C	-	0.4	4	293 – 323	1
Mamedov <i>et al.</i>	1975	C	99.4	2	124	323 – 548	1 – 400
Kashiwagi and Makita	1982	TC	99	2	60	298 – 348	1 – 1094
Abdullaev and Akhundov	1983	C	-	2	27	473 – 673	1 – 38
Dymond and Robertson	1985	C	99	1	6	298 – 393	P _{Sat}
Serrano <i>et al.</i>	1990	C	99.98	0.4	4	288 – 303	1
Vogel and Hendl	1992	C	99.9	0.3	66	383 – 633	0.08 – 2
Et-Tahir <i>et al.</i>	1995	FB	99	2	12	313 – 353	200 – 1000
Exarchos <i>et al.</i>	1995	C	99.5	0.4	5	293 – 313	1

C – Capillary; FB – Falling Body; RB – Rolling Body; TC – Torsional Crystal

Figure 1 graphically represents the temperature and pressure range of the measurements outlined in Table 1 differentiating between primary and secondary data. It shows that the primary data cover a wide range of temperatures and pressures of interest. The vapour phase extend through the temperature range (338 to 613)

K at pressures up to 25 bar. The liquid phase temperature, ranges from (288 to 548) K with pressures up to 1100 bar. The supercritical region extends to temperature ranging from (623 to 673) K at pressures up to 38 bar.

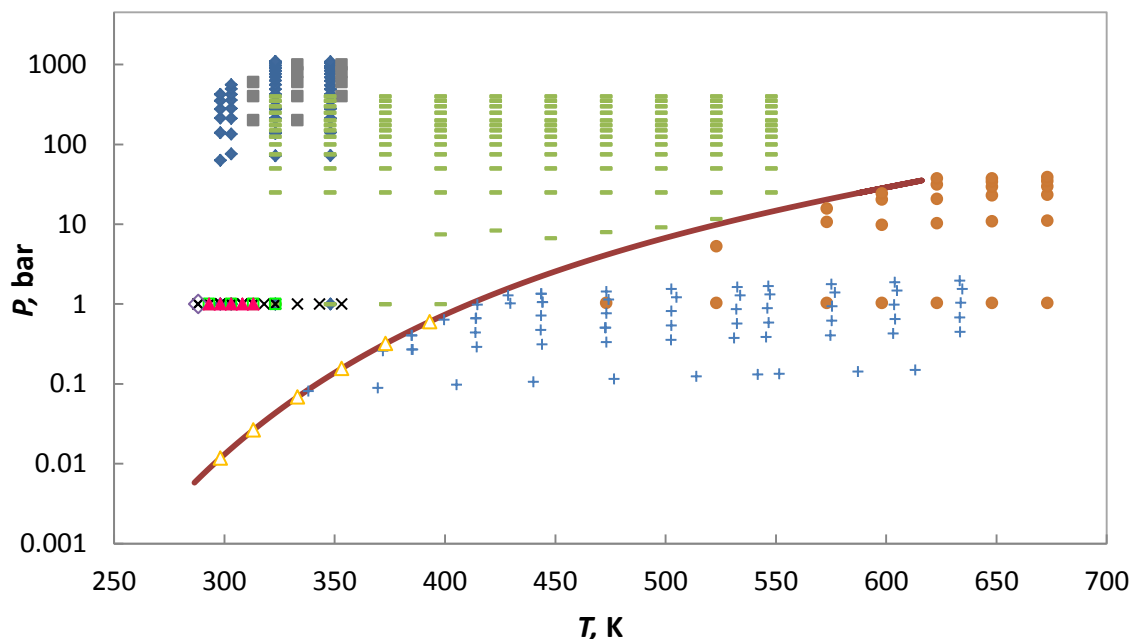


Figure 1 – Distribution of the available experimental viscosity data of *p*-xylene. Primary Data: (→) Mamedov and Panchenkov (1955) and Mamedov *et al.* (1968, 1975), (□) Nissema and Koskenniska (1972), (♦) Kashiwagi and Makita (1982), (●) Abdullaev and Akhundov (1983), (△) Dymond and Robertson (1985), (◇) Serrano *et al.* (1990) (+) Vogel and Hendl (1992), (■) Et-Tahir *et al.* (1995), (▲) Exarchos *et al.* (1995), Secondary Data: (×), VLE: (—)

Experimental measurements of viscosity are usually reported at a given temperature and pressure, where experimentally determined densities are given. When developing a viscosity correlation that utilises the existing theory for guidance, temperature and density are the natural variables. As a result, an EOS is required to convert (T, P) pairs into corresponding (T, ρ) pairs. Using EOS-generated density offers supplementary level of consistency, further reducing the uncertainty of the developed correlation. For the purpose of this work, the latest reference EOS developed by Zhou *et al.* (2012) has been used, it covers the thermodynamic space from the triple point to 673 K, and up to 4000 bar. Uncertainties in density are estimated to be $\pm 0.2\%$ in the liquid region and $\pm 1.0\%$ elsewhere (Zhou *et al.*, 2012).

Methodology and Analysis

When developing correlations of transport properties, it is beneficial to incorporate theoretical guidance to the correlation functional form in terms of temperature and density. Viscosity η is expressed as the sum of four contributions (Millat *et al.*, 2005):

$$\eta = \eta_0(T) + \eta_1(T)\rho + \Delta\eta(\rho, T) + \Delta\eta_c(\rho, T) \quad (1)$$

where ρ is the molar density, T is the temperature and the different contributions to viscosity, η_0 , η_1 , $\Delta\eta$ and $\Delta\eta_c$ are the zero-density viscosity, the initial-density coefficient, the residual viscosity and the critical enhancement, respectively. Due to lack of experimental data within the critical enhancement region its effect was neglected. Breaking down the viscosity contribution, offers a better analysis of the individual effects. Theories at present, give sufficient understanding of the low density region, dilute-gas regime and behaviour near the critical point, where the density variations exhibits a divergence of the viscosity (Assael *et al.*, 2014).

The Zero-Density Limit

At the zero-density limit, viscosity is challenging to measure directly through experimentation. Therefore, measured data at the low density region are extrapolated at a given isotherm. The values are then fitted to the linear equation (Millat *et al.*, 2005):

$$\eta = \eta_0 + \eta_1\rho \quad (2)$$

Vogel and Hendl (1992) were the only authors which reported viscosity of *p*-xylene at pressures below 3 bar, and covered a wide temperature range from (383 - 633) K. A viscometer which fulfils the requirements to be accepted as primary data was used, justifying its usage to represent the zero-density limit viscosity.

The standard relationship in kinetic theory is used to represent the viscosity in the zero-density limit, $\eta_0(T)$, given by:

$$\eta_0(T) = \frac{1}{4} \sqrt{\frac{k_B \sqrt{MT}}{\pi N_A S_\eta}} = 0.22005 \frac{\sqrt{T}}{S_\eta} \quad (3)$$

where T is the temperature in Kelvin, M is the molar mass, S_η is the effective collision cross-section in nm^2 and $\eta_0(T)$ in $\mu\text{Pa}\cdot\text{s}$. The numerical constant in Eq. (3) was obtained using the recommended values of fundamental constants (Mohr *et al.*, 2012) and relative molecular mass of 106.165 (Wieser and Coplen, 2011).

Zero-density viscosity is usually fitted through using three terms which includes an energy scaling parameter, ε/k , a size scaling parameter, σ , and finally an elected functional form for cross-sectional area, S_η . Typically, the two functional forms used is firstly the Lennard-Jones model which approximates the interactions between molecules as an effective spherical Lennard-Jones (12-6) potential (Neufeld *et al.*, 1972). The second is the universal correlation, which arises from implementing a universal correlation for S_η utilising experimental data. The benefit of these functional forms is the ability to extrapolate viscosities reasonably, out of the measured data range. Figure 2 shows the result of implementing Vogel and Hendl (1992) data with the Lennard-Jones model and universal correlation. It can be concluded that with careful consideration of the scaling parameters (ε and σ) the two functional forms can reproduce the data within systematic deviations of 0.65%, which is greater than double the claimed uncertainty of the measured data.

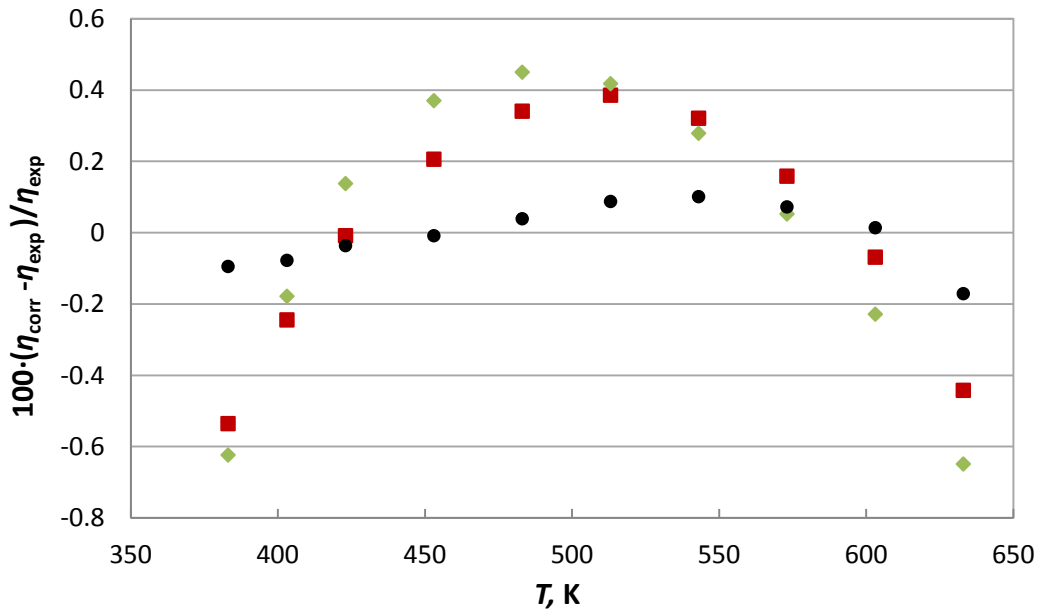


Figure 2 – Percentage deviations $[100 (\eta_{corr} - \eta_{exp})/\eta_{exp}]$ from the experimental data of Vogel and Hendl (1992) in the limit of zero-density, of the values calculated by: (●) Empirical; (■) Lennard-Jones Correlation; (◆) Universal Correlation

This result indicates that for aromatic molecules the universal correlation and Lennard-Jones model cannot reproduce the zero-density viscosity within the experimental uncertainty. In order to reproduce accurately the zero-density viscosity within the experimental uncertainty, an empirical approach has been adopted by obtaining experimental values of S_η from fitting each primary data point to the form:

$$\ln(S_\eta/nm^2) = A_0 + \frac{B_0}{T} + \frac{C_0}{T^2} \quad (4)$$

where A_0 , B_0 and C_0 are adjustable fitting coefficients obtained using nonlinear least-square (nls) techniques in R statistical software (R Development Core Team, 2008). Table 2 provides the values obtained and Figure 2 illustrates that the empirical correlation fits the primary data within 0.17%, substantially below the claimed uncertainty region of 0.3%.

Table 2 – Coefficients for the Empirical Fitting of the Zero-Density Limit Viscosity, Eq.(4)

A_0 [-]	B_0 [K]	C_0 [K ²]
-1.4933	473.2	-57033

The Initial Density Dependence

In the vapour phase, at subcritical conditions, a viscosity trend showing an initial increase or decrease with increasing density before viscosity increases at higher densities is witnessed below a particular temperature (Friend and Rainwater, 1984). A model that accounts for this behaviour of the initial-density coefficient, η_1 , is in terms of the second viscosity virial coefficient, B_η , defined by (Millat *et al.*, 2005):

$$\eta_1(T) = B_\eta(T) \eta_0(T) \quad (5)$$

where η_1 is in $\mu\text{Pa}\cdot\text{s}\cdot\text{L}\cdot\text{mol}^{-1}$ and B_η in $\text{L}\cdot\text{mol}^{-1}$. Proposed schemes to describe the second viscosity virial coefficient were initially founded on models of moderately dense gas as mixture of monomers and dimers which interact analogous to the LJ (12-6) potential. However, currently it is based on universal correlations made with the careful consideration of the experimental data and theory (Friend and Rainwater, 1984).

Out of the authors which measured data in the vapour phase, only data of Vogel and Hendl (1992) were sufficiently detailed to allow for the development of an initial-density correlation. Hence, it has been used as the primary dataset and tested with the universal correlation using optimal choice of scaling parameters ε and σ . It was found to predict values recorded by Vogel and Hendl (1992) outside the range of claimed uncertainty. For greater accuracy an empirical approach was undertaken with the initial density dependence shown by the functional form:

$$\eta_1(T)\rho = \left(A_1 + \frac{B_1}{T} + \frac{C_1}{T^2} \right) \rho \quad (6)$$

where A_1 , B_1 and C_1 are adjustable fitting coefficients and ρ is the molar density in $\text{mol}\cdot\text{L}^{-1}$. The Vogel and Hendl (1992) primary dataset contains 66 data points fitted to Eq. (6), which meant the zero-density correlation was extrapolated to 338 K to include the 11 data points in this temperature range. Table 3 provides the fitted coefficients obtained with Figure 3 showing the deviations of the initial density correlation from experimental data. An illustrated fit within 0.25% was within the claimed experimental uncertainty of 0.3%. It can be concluded that the extrapolation of the zero-density correlation to 338 K is valid because the 11 data points in the temperature range (338 to 633) K was predicted within the experimental uncertainty.

Table 3 – Coefficients for the Empirical Fitting of the Initial Density Dependence, Eq.(6)

A_1 [$\mu\text{Pa}\cdot\text{s}\cdot\text{L}\cdot\text{mol}^{-1}$]	B_1 [$\mu\text{Pa}\cdot\text{s}\cdot\text{K}\cdot\text{L}\cdot\text{mol}^{-1}$]	C_1 [$\mu\text{Pa}\cdot\text{s}\cdot\text{K}^2\cdot\text{L}\cdot\text{mol}^{-1}$]
13.2814	-10862.4	1664060

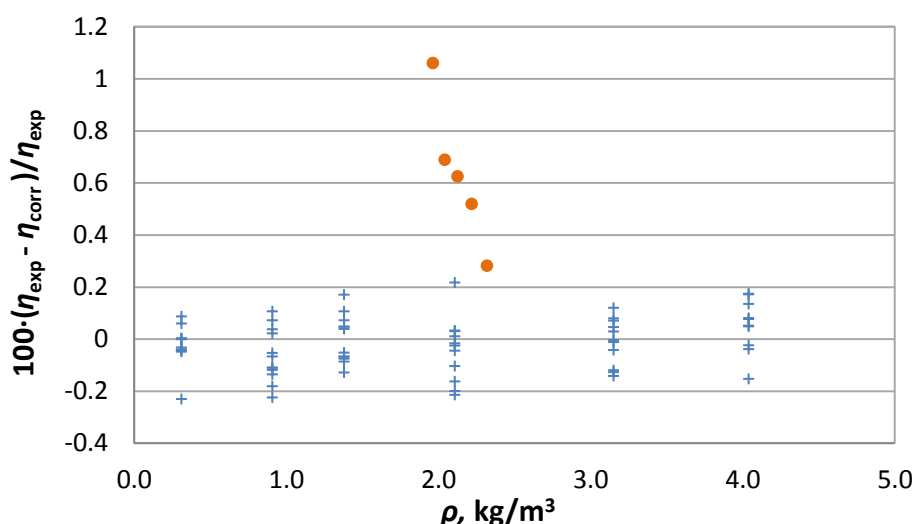


Figure 3 – Percentage deviations $[100(\eta_{corr} - \eta_{exp})/\eta_{exp}]$ of the available experimental data in the vapour phase at pressures below 2 bar from the calculated values: (o) Abdullaev and Akhundov (1983), (+) Vogel and Hendl (1992)

Figure 3 shows the deviation of all the datasets available in the vapour phase from the correlation given by Eqs. (2-6). Both datasets show deviations within their claimed uncertainty of 2 % and 0.3 %, respectively, with no evident systematic trend either in density or temperature. It also can be noted that the data of Abdullaev

and Akhundov (1983) extends Vogel and Hendl (1992) in the supercritical region by 40 K and the correlation was still able to extrapolate outside of the primary data range and produce values within the experimental uncertainty. Therefore, it can be stated that the developed correlation has the correct temperature dependence when extrapolated to lower and higher temperatures.

On the basis of the agreement with the primary data set, an estimated combined uncertainty with a coverage factor of 2 to the viscosity correlation in the vapour phase, below 2 bar, of 0.25% in the temperature range (338 to 633) K. Outside this range an estimated uncertainty increase to 1% at 673 K.

The Residual Viscosity

There is limited theoretical guidance for the residual viscosity contribution. Thus, the availability of accurate experimental data which can cover a large range of temperature and pressure is crucial to develop a valid correlation. The first stage of choosing primary data was to collate and compare the high ranged temperature and pressure data, to perform an initial fitting. The second stage was then to add the ambient and saturation data to the fitting.

Amongst the available viscosity datasets only 5 cover a large range of temperature and pressure. Mamedov *et al.* (1968, 1975) measurements were obtained using a capillary viscometer. Kashiwagi and Makita (1982) used a Torsional Crystal and Et-Tahir *et al.* (1995) used a Falling Body viscometer. The primary dataset covered the temperature range (293 to 548) K and pressures from 1 bar up to 1100 bar.

With the aim of performing the comparison between different datasets, a quadratic polynomial fit in density to Kashiwagi and Makita (1982) data was used as a base line. Figure 4 clearly shows that Mamedov *et al.* (1968, 1975) exhibits a systematic deviation from the primary data at lower densities. However, this difference is within the experimental accuracy in the order of 2%.

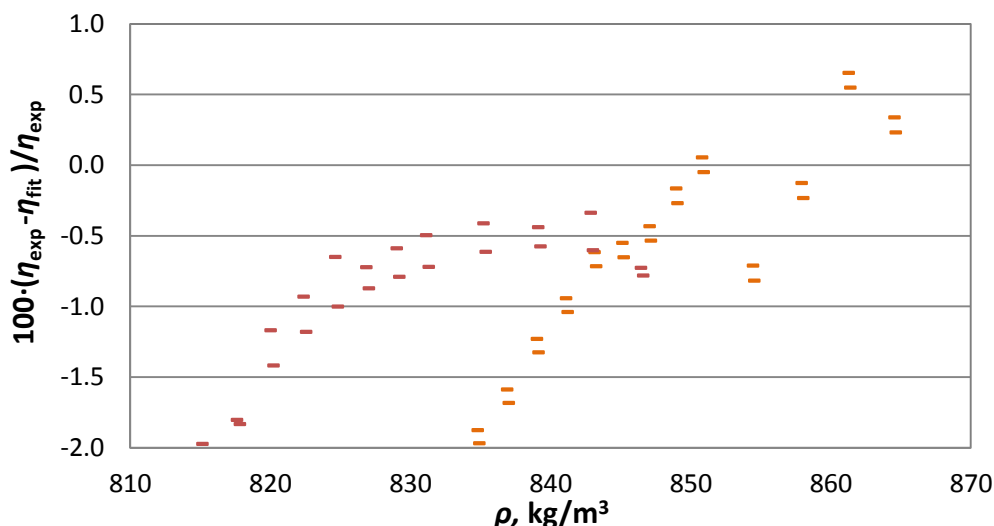


Figure 4 – Percentage deviations $[100 (\eta_{exp} - \eta_{fit}) / \eta_{exp}]$ of the primary experimental viscosity data at 323 K and 348 K from the quadratic fit in density to Kashiwagi and Makita (1982) data. 323 K data: (–) Mamedov *et al.* (1968, 1975). 348 K data: (–) Mamedov *et al.* (1968, 1975)

Analysis of the data Kashiwagi and Makita (1982) and Mamedov *et al.* (1968, 1975) indicated agreement between these datasets within the claimed uncertainty over the whole range of temperatures and pressures which justified their inclusion within the primary dataset.

The primary dataset was accompanied by four sets of viscosity measurements of liquid *p*-xylene at atmospheric pressure covering the temperature range (288 to 353) K and one set of measurements along the saturation line from the temperature range (298 to 393) K. In summary, 351 data points covering the temperature range (298 to 548) K and pressures up to 1100 bar measured in 3 different viscometer types, were used as primary data for development of the residual viscosity contribution.

All the viscosity data were converted from the $\eta(T,P)$ to $\eta(T,\rho)$ using the EOS of Zhou *et al.* (2012). When removing the zero-density and initial density dependence contributions, Eqs. (4 and 6) respectively, from the residual viscosity the typical features of $\eta(T,\rho)$ is shown. This is the viscosity exponential-like increase at temperatures and densities near the solidification line, also no existing data within the 2-phase region. This can cause the viscosity correlation to display non-monotonic behaviour within this region. The fitting has been constrained to ensure that the correlation is continuous and a monotonically increasing function of density at all isotherms. Therefore, this gives the possibility for a reference correlation and the ability to represent *p*-xylene in calculating mixture viscosity in corresponding states or VW method (Vesovic and Wakeham, 1989).

The residual viscosity is presented here as a function in reduced density, $\rho_r = \rho/\rho_c$ and reduced temperature, $T_r = T/T_c$,

$$\Delta\eta(\rho, T) = \rho_r^{2/3} \sum_{i=1.5,2,3,4,5,11} (D_i \rho_r^i) + \frac{\rho_r^{2/3}}{T_r^{0.5}} \sum_{i=1.5,11,15} (E_i \rho_r^i) \quad (7)$$

where D_i and E_i are adjustable coefficients. In this instance, fractional powers have been used to allow more flexibility in fitting the experimental data, for smooth 2-phase representation. Residual viscosity of supercritical fluids is independent temperature (Vesovic *et al.*, 1998). The D_i terms in Eq. (7) accounts for this behaviour. Liquids, however, exhibit a strong temperature dependence (Assael *et al.*, 1992). The E_i term accounts for the liquid viscosity behaviour. Avgeri *et al.* (2014) proposed functional form suggested from the hard-sphere model, $\Delta\eta(\rho, T) = \rho_r^{2/3}/T_r^{1/2}$ which was employed in this correlation providing the best results.

Table 4 shows the optimal coefficients for Eq. (7) which were obtained using the R software for statistical computing (R Development Core Team, 2008) to fit all the primary data. The critical temperature, T_c , 616.168 K and critical density, ρ_c , 2.69392 mol·L⁻¹ of *p*-xylene were taken from Zhou *et al.* (2012).

Table 4 – Coefficients for the Representation of the Residual Viscosity, Eq. (7)

i	D_i	E_i
1.5	122.919	15.337
2	-282.329	-
3	279.348	-
4	-146.776	-
5	28.361	-
11	-0.004585	-0.0004382
15	-	0.00002307

Figure 5 shows the agreement with the experimental data in the liquid region for temperatures from (298 to 548) K and pressures from saturation to 1100 bar. The experimental data are reproduced by the present correlation within 2.7 % with no systematic data trend. The data of Dymond and Robertson (1985) measured along the saturation line are reproduced within 1 %, within the claimed uncertainty of the data. Nissema and Koskenniska (1972) exhibit average absolute deviation (AAD) of 0.3 %, bias of 0.3 % and maximum deviation of 0.7 %, just above the claimed uncertainty. Overall, the developed correlation is able to reproduce the data mostly within 2 % with less than 2 % of the primary data outside this threshold.

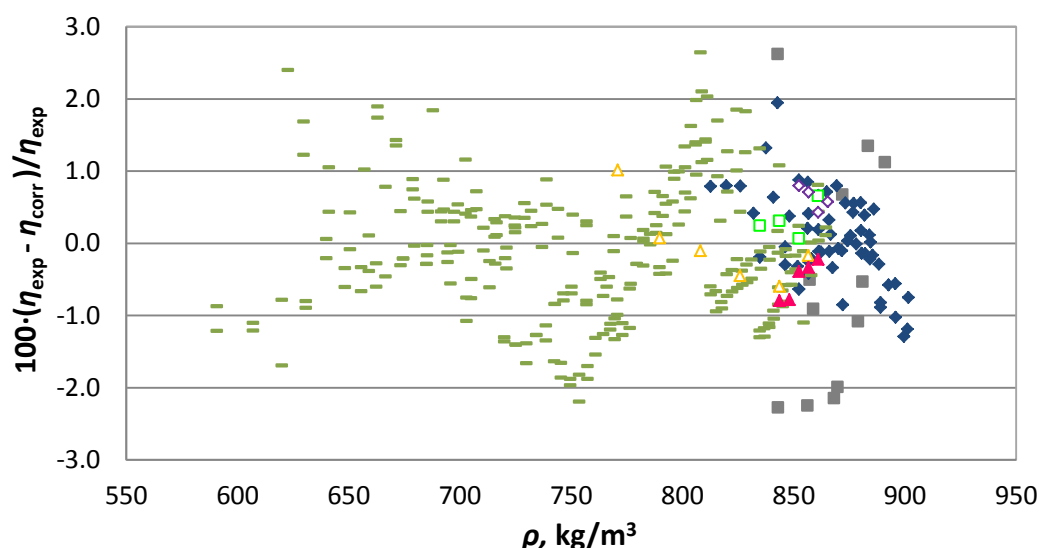


Figure 5 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})/\eta_{exp}]$ of primary experimental viscosity data in the liquid region: (–) Mamedov and Panchenkov (1955) and Mamedov *et al.* (1968, 1975), (□) Nissema and Koskenniska (1972), (♦) Kashiwagi and Makita (1982), (Δ) Dymond and Robertson (1985), (◇) Serrano *et al.* (1990), (■) Et-Tahir *et al.* (1995), (▲) Exarchos *et al.* (1995)

Figure 6 compares the agreement of the primary data for Kashiwagi and Makita (1982) and Mamedov *et al.* (1968, 1975) at the same isotherms. Both claimed uncertainty of 2 %, however, they used different

viscometers (See Table 1). Kashiwagi and Makita (1982) data is mainly over predicted exhibiting systematic deviation at the higher densities at 348 K, whereas Mamedov *et al.* (1968, 1975) are mainly under predicted with systematic deviation at lower densities for both isotherms 323 K and 348 K. At 348 K, there is up to 1.5 % difference in the predicted viscosity deviation of the authors. Despite these systematic differences, the developed correlation is shown to reproduce the data within the claimed uncertainty of 2 %.

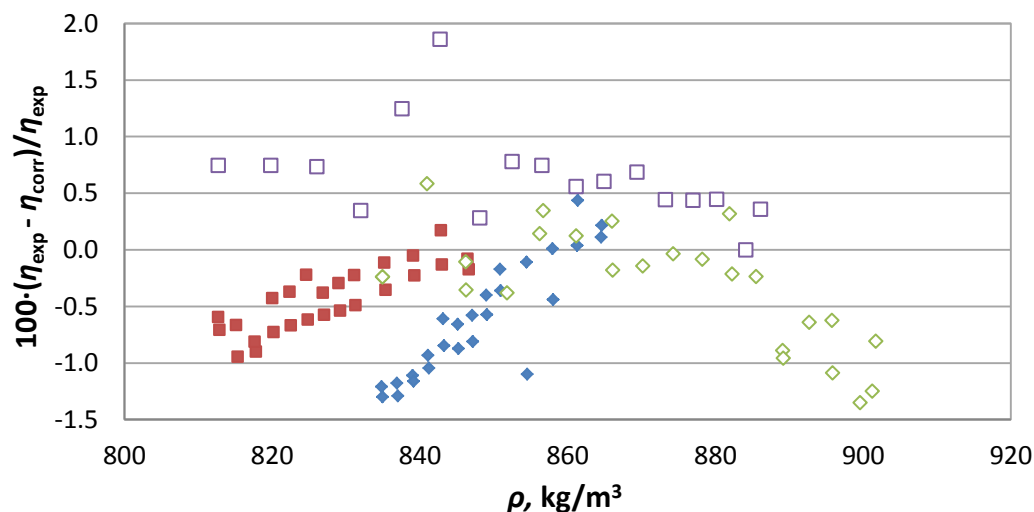


Figure 6 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})/\eta_{exp}]$ of the primary experimental viscosity data at 323 K and 348 K in the liquid region. 323 K data: (\diamond / \blacklozenge) Kashiwagi and Makita (1982)/Mamedov *et al.* (1968, 1975). 348 K data: (\square / \blacksquare) Kashiwagi and Makita (1982)/Mamedov *et al.* (1968, 1975)

Figure 7 illustrates the agreement of the developed viscosity correlation with the primary experimental data at atmospheric pressure, that cover the temperature range (298 to 373) K in the liquid phase. All the data are reproduced within 1.5 % with the exception of a single datum of Mamedov and Panchenkov (1955) at 353 K. However, taking into account that these measurement were taken at room temperature in different laboratories, it can be concluded that the suggested correlation represents the primary experimental data well. Nissema and Koskenniska (1972), Serrano *et al.* (1990) and Exarchos *et al.* (1995) claimed low uncertainty of 0.4 %, observing Figure 7 emphasises a good agreement with the correlation as it predicts close to this claimed uncertainty. Dymond and Robertson (1985) data does show a systematic deviation at the lower densities, though the predictions are within the claimed uncertainty of 1 %.

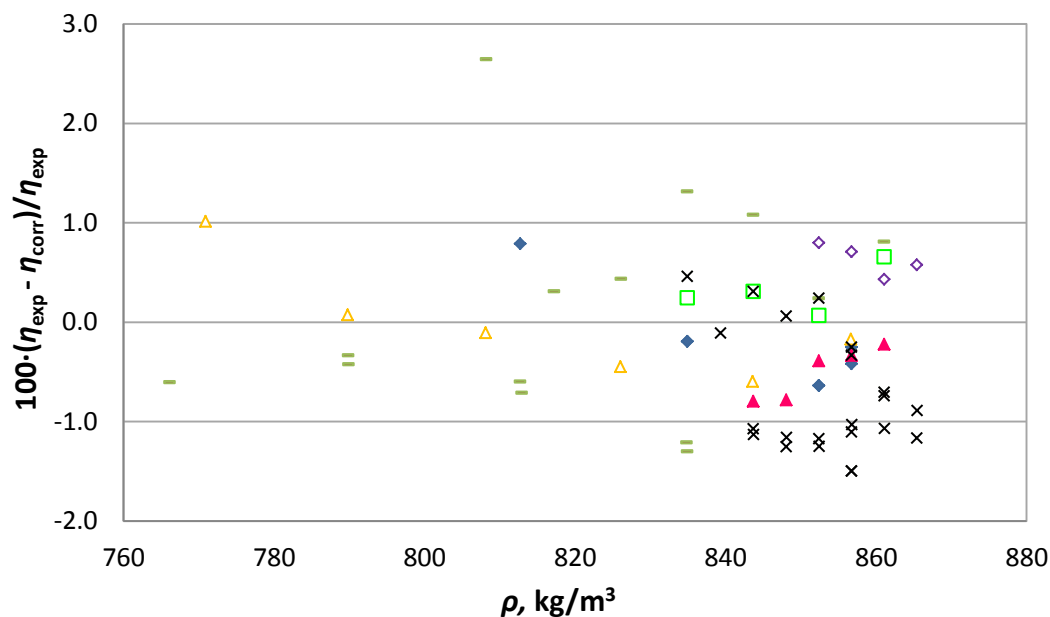


Figure 7 – Percentage deviations $[100(\eta_{exp} - \eta_{corr})/\eta_{exp}]$ of primary experimental viscosity data measured at 1 bar: (–) Mamedov and Panchenkov (1955) and Mamedov *et al.* (1968, 1975), (\square) Nissema and Koskenniska (1972), (\blacklozenge) Kashiwagi and Makita (1982), (Δ) Dymond and Robertson (1985), (\diamond) Serrano *et al.* (1990), (\blacksquare) Et-Tahir *et al.* (1995), (\blacktriangle) Exarchos *et al.* (1995)

Table 5 – Evaluation of the *p*-Xylene Viscosity Correlation against the Primary Experimental Data

Authors	Year Publ.	AAD (%)	Bias (%)	MD (%)
Mamedov and Panchenkov	1955	1.0	1.0	2.6
Mamedov <i>et al.</i>	1968	0.8	-0.1	2.4
Nissema and Koskenniska	1972	0.3	0.3	0.7
Mamedov <i>et al.</i>	1975	0.7	-0.2	-2.2
Kashiwagi and Makita	1982	0.5	0.0	1.9
Abdullaev and Akhundov	1983	1.0	0.5	2.6
Dymond and Robertson	1985	0.4	0.0	1.0
Serrano <i>et al.</i>	1990	0.6	0.6	0.8
Vogel and Hendl	1992	0.1	0.0	-0.2
Et-Tahir <i>et al.</i>	1995	1.5	-0.5	2.6
Exarchos <i>et al.</i>	1995	0.5	-0.5	0.8
Entire Primary Data Set		0.6	0.0	2.6

$$AAD = 100/N \sum |(\eta_{exp} - \eta_{corr})/\eta_{exp}|; \quad Bias = 100/N \sum (\eta_{exp} - \eta_{corr})/\eta_{exp}$$

Table 5 summarizes the agreement between the primary data and the proposed viscosity correlation, Eqs. (1-4 and 6-7), for *p*-xylene in the vapour, liquid and supercritical regions. The correlation reproduces the entire primary data with the average absolute deviation (AAD) of 0.6 %, zero bias and maximum deviation (MD) of 2.7 %

Overall Viscosity Correlation

The viscosity correlation of *p*-xylene as a function of temperature and density is represented by Eqs. (1-4 and 6-7), with the coefficients provided in Table 2-4. The correlation is valid from the lower temperature range of 288 K to the upper limit which is pressure dependent. For densities coinciding of pressures below 3 bar the viscosity correlation is valid up to 673 K, whereas at higher pressures the correlation is valid till 548 K.

Figure 8 illustrates the behaviour of the viscosity correlation as a function of density along isotherms 300 K and 600 K. At higher densities a steep increase in viscosity is observed. It can be also seen that the correlation is well-behaved within the 2-phase region, where no data is available to constrain the correlation. For all isotherms, monotonic behaviour is exhibited. Therefore, the correlation is suitable for a corresponding states correlation for aromatic hydrocarbons or to represent a specific component in calculating mixture viscosity in VW model (Vesovic and Wakeham, 1989).

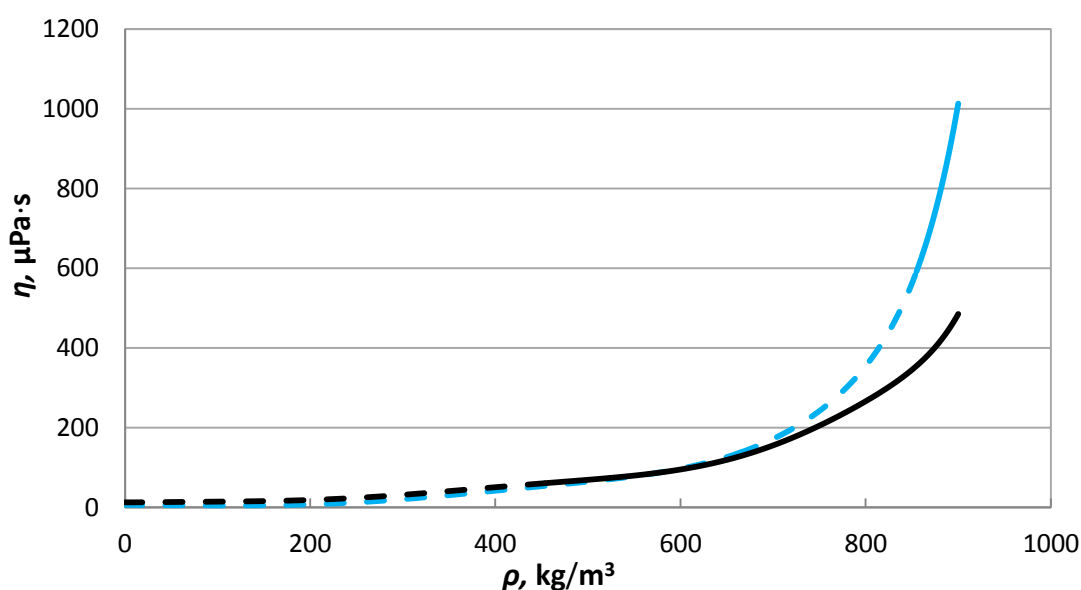


Figure 8 – Viscosity of *p*-xylene as a function of density along isotherms. 300 K: (—) liquid phase, (---) 2-phase region. 600 K: (—) liquid phase, (---) 2-phase region.

Computer-Program Verification

Table 6 is provided to assist the user in the computer-program verification. The viscosity calculations are based on the tabulated temperatures and densities.

Table 6 – Sample Points for Computer Verification of the Correlation Equations

T [K]	ρ [kg/m ³]	η [μ Pa·s]	T [K]	ρ [kg/m ³]	η [μ Pa·s]	T [K]	ρ [kg/m ³]	η [μ Pa·s]
300	0	6.604	400	0	8.573	600	0	12.777
300	2.5	6.504	400	2.5	8.495	600	2.5	12.776
300	700	171.936	400	700	157.208	600	700	155.664

MODELLING THE VISCOSITY OF AROMATIC-ALKANE BINARY MIXTURES

This section describes the VW method to predict viscosity of benzene-alkane mixtures. The choice of density to compute the pure species parameters has been investigated. A recommendation is made and the results for benzene-alkane mixtures are discussed.

Theory and Methodology

Enskog's expression describes the viscosity of pure fluid containing rigid spheres of diameter σ (Chapman and Cowling, 1952):

$$\eta = \eta_0 \left(\frac{1}{\chi} + \alpha\rho + \frac{1}{\beta} \alpha^2 \rho^2 \chi \right) \quad (8)$$

where β is constant $(1/4 + 3/\pi)^{-1}$ and χ is the radial distribution function. α is a parameter, proportional to the excluded volume per molecule, V_{excl} :

$$\alpha = \frac{8}{15} N_A \pi \sigma^3 = \frac{2}{5} N_A V_{excl} \quad (9)$$

When non-spherical molecules are involved, linear molecules are modelled as equally sized tangentially joined and rigid segmented spheres. Viscosity of fluids made up of C chains with m segments can be modelled in the dense-fluid region consisting of mC hard spheres, referred as segmented fluids, given by a modification of Eq. (8), (de Wijn *et al.*, 2008):

$$\eta = \tilde{\eta}_0 \left(\frac{1}{\tilde{\chi}} + \tilde{\alpha}\tilde{\rho} + \frac{1}{\tilde{\beta}} \tilde{\alpha}^2 \tilde{\rho}^2 \tilde{\chi} \right) \quad (10)$$

where the modified quantities (marked with a tilde) are defined on a per segment basis:

$$\tilde{\rho} = \rho m \quad (11)$$

$$\frac{\tilde{\alpha}}{\tilde{\alpha}_{segment}} = 1 + \frac{3}{2}(m-1) + \frac{3}{8}(m-1)^2 \quad (12)$$

$$\tilde{\eta}_0 = \eta_0 \tilde{\chi}_0 = \eta_0 \left(1 - \frac{5}{8} \left(\frac{m-1}{m} \right) \right) \quad (13)$$

where $\tilde{\alpha}_{segment}$ is the excluded volume of the free segment. When $m = 1$ the fluid reproduces the hard sphere fluid behavior. The reader is referred to de Wijn *et al.* (2012) for the equations used to calculate viscosity mixtures.

Estimation of Pure Species Parameters

To predict mixture viscosities, first it is required to estimate the parameters for each component in the mixture, where empirical correlations are conventionally used. However, their application ranges from the regions of experimental data placing limitations to the robustness. In this study the empirical correlation used for benzene was Avgeri *et al.* (2014) and for n-alkanes Assael *et al.* (1992), however due to reason explored later in the report, for n-hexane Lemmon *et al.* (2013) was used.

The radial distribution function at contact, $\tilde{\chi}$, can be calculated from viscosity by inverting the quadratic form of the effective pure species properties, Eq. (10), (Vesovic and Wakeham, 1989):

$$\tilde{\chi}^{\pm} = \frac{\beta}{2\tilde{\rho}_i\tilde{\alpha}_i} \left[\left(\frac{\eta}{\tilde{\rho}_i\tilde{\alpha}_i\tilde{\eta}_{0i}} - 1 \right) \pm \sqrt{\left(\frac{\eta}{\tilde{\rho}_i\tilde{\alpha}_i\tilde{\eta}_{0i}} - 1 \right)^2 - \frac{4}{\beta}} \right] \quad (14)$$

To ensure physical behavior of χ , Sandler and Fiszdon (1979) showed that to switch from $\tilde{\chi}^{\pm}$ path to the $\tilde{\chi}^{\pm}$ path of the solution at a particular density defined $\tilde{\rho}_i^* = m_i\rho_i^*$, where the switch over density, ρ_i^* , is obtained from:

$$\left(\frac{\partial \eta_i}{\partial \rho} \right) = \frac{\eta_i^*}{\rho_i^*} \quad (15)$$

Eq.(16) makes $\tilde{\alpha}_i$ a parameter dependent on temperature,

$$\tilde{\alpha}_i = \frac{\eta_i^*}{\rho_i^*\tilde{\eta}_{0i}} \left(1 + \frac{2}{\sqrt{\beta}} \right)^{-1} \quad (16)$$

The parameters $\tilde{\alpha}_i$ and $\tilde{\chi}_i$ are calculated at the mixture temperature, but there are multiple options for the density at which $\tilde{\chi}_i$ is calculated. Vesovic and Wakeham (1989) proposed equal molar density, whereas de Wijn *et al.* (2012) used reduced density for VW-chains. However, *n*-alkanes required conditions at unrealistic densities producing negative viscosities. Therefore, same mass density was employed which provided generally accurate, well-behaved values of pure *n*-alkane viscosity. With the experimental data acquired for this investigation, most pure species prediction was within the range of the claimed uncertainty.

Estimation of Mixture Interaction Parameters

The mixture interaction parameters ($\tilde{\alpha}_{ij}, \tilde{\chi}_{ij}, \tilde{\eta}_{0ij}$) are obtained from pure species parameters by employing the mixing rules recommended by de Wijn *et al.* (2012). A number of mixing rules to evaluate $\tilde{\chi}_{ij}$ are available and descriptions can be found in the appendix of de Wijn *et al.* (2012). For this study, Anstaz 5 was used and analyzed in a later section of this report (also see Appendix C).

Experimental Data

The data for binary mixtures of benzene + *n*-C₆, *n*-C₈, *n*-C₁₀, *n*-C₁₂ or *n*-C₁₆ were collected for analysis. All authors reported experimental densities which were used for the VW model. The experimental technique, temperatures, pressures and claimed uncertainty are recorded in Table 7. The experimental data is all reported at 298 K and 1 bar.

Table 7 – Experimental Data for Mixture Viscosities

Authors	Year Publ.	Technique Employed	No. of Data	Phase	Temperature (K)	Pressure Range (bar)	MD (%)
Benzene + <i>n</i>-C₆							
Awwad <i>et al.</i>	1986	C	12	L	298	1	3.9
Lal <i>et al.</i>	2000	C	16	L	298	1	1.7
Benzene + <i>n</i>-C₈							
Awwad <i>et al.</i>	1986	C	11	L	298	1	13.7
Benzene + <i>n</i>-C₁₀							
Awwad <i>et al.</i>	1986	C	12	L	298	1	13.4
Lal <i>et al.</i>	2000	C	16	L	298	1	12.6
Benzene + <i>n</i>-C₁₂							
Awwad <i>et al.</i>	1986	C	12	L	298	1	13.2
Benzene + <i>n</i>-C₁₆							
Awwad <i>et al.</i>	1986	C	12	L	298	1	21.2
Lal <i>et al.</i>	2000	C	16	L	298	1	20.6

C – Capillary; FB – Falling Body; RB – Rolling Body; TC – Torsional Crystal

During the process of the work, it was observed that the reference correlation for benzene (Avgeri *et al.*, 2014) does not extrapolate well and becomes negative at very high densities. This constraint limits the conditions of applicability of the VW method, especially for mixtures with *n*-C₁₆.

Results and Discussion

In the study of the application of the VW method, the procedure to estimate the pure species parameters was investigated through different density schemes. Furthermore, results from the for benzene-alkane mixtures viscosity predictions are discussed.

Effect of Density on the Parameters of Pure Species

The VW method defines the temperature and density at which pure species parameters are calculated. Figure 9 illustrates the effect of altering the density choice on a benzene + *n*-C₆ mixture from Lal *et al.* (2000). This includes equal molar density of spheres, equal reduced density and equal segment density. Equal reduced density reproduced the data with a maximum error of 1.7%, within the claimed accuracy of the experimental data of 2%. With the other options, errors ranging from 3% to 70 % were realized. For mixtures with heavier *n*-alkanes (shown in Appendix C) it was observed that although the deviations in the prediction increase outside the uncertainty claimed by the authors, equal reduced density minimizes the deviations, which justifies the conclusion that equal reduced density best represents density at which the pure species parameters are calculated for benzene-alkane mixtures.

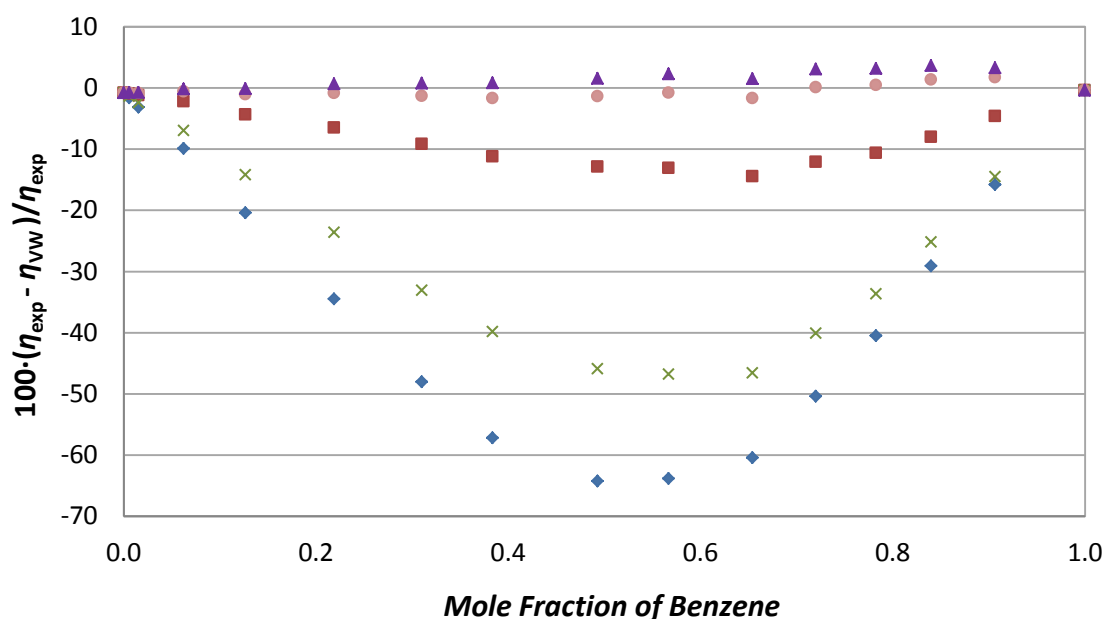


Figure 9 – Percentage deviations $[100(\eta_{exp} - \eta_{VW})/\eta_{exp}]$ of different pure species conditions on the VW method predictive capabilities for the mixture of benzene with *n*-C₆ of Lal *et al.* (2000). (♦) Equal molar density, (■) Equal segment density, (×) Equal mass density, (●) Equal reduced density, (▲) Equal reduced density and temperature

A further study was done on the effect of the mixing rule on the VW method prediction of benzene-alkane mixture viscosity (shown in Appendix C). It was observed that it is sensitive to alterations in the mixing rule used for χ_{ij} . Moreover, chain length is a factor that may determine the mixing rule used. This indicates further testing in this area is required which was proposed by de Wijn *et al.* (2012) and Tariq (2013) who witnessed similar behaviors for mixtures with *n*-alkane and cyclic molecules respectively.

It was observed that for mixtures with alkanes heavier than *n*-C₆, the parameters are calculated within the 2-phase region. This is because the critical density of *n*-C₆ is less than that of benzene, 2.80 mol·L⁻¹ and 2.86 mol·L⁻¹ respectively. Correlations proposed by Lemmon *et al.* (2013) was shown to not behave monotonically within the 2-phase region. It was founded that Assael *et al.* (1992) which uses the hard sphere model, exhibiting a more realistic 2-phase region trend, therefore it was used for alkanes heavier than *n*-C₆. Problems arise with mixtures of *n*-C₁₆ due to the benzene correlation becoming negative at very high densities.

Benzene-Alkane Mixtures

Figure 10 illustrates the results for the mixture of benzene with *n*-C₆. The VW method reproduce Lal *et al.* (2000) data with a MD of 1.7%, following a similar trend within the experimental uncertainty. Awwad *et al.* (1986) observes a MD of 4.1% which is less accurate, this due to *n*-C₆ pure species viscosity extending outside the range of the correlation uncertainty proposed by Lemmon *et al.* (2013). This will inevitably affect the whole range of data from the author.

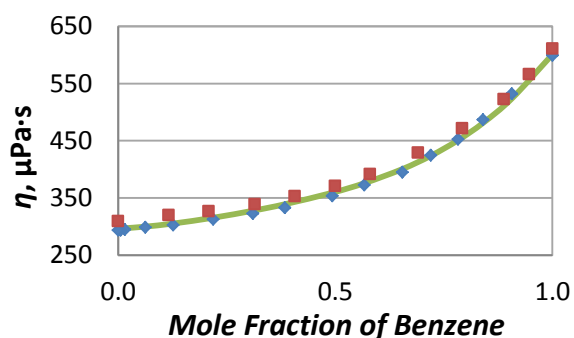


Figure 10 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with $n\text{-C}_6$. Experimental data: (♦) Lal *et al.* (2000), (■) Awwad *et al.* (1986). VW: (—)

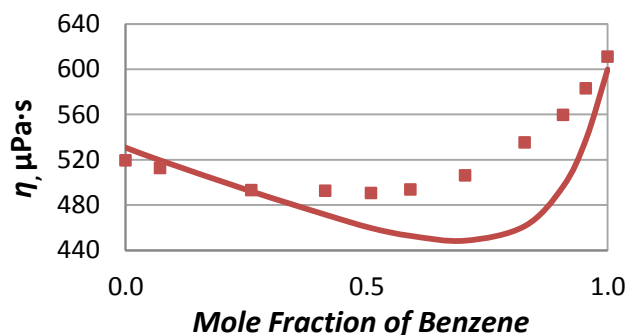


Figure 11 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with $n\text{-C}_8$. Experimental data: (■) Awwad *et al.* (1986). VW: (—)

For mixtures of benzene + $n\text{-C}_8$, $n\text{-C}_{10}$ or $n\text{-C}_{12}$ a pattern is observed with the VW method predicting viscosities at a similar trend to the experimental data, shown in Figure 11 to Figure 13. As the benzene content becomes richer, mixture viscosity is under-predicted. In benzene + $n\text{-C}_8$ or $n\text{-C}_{10}$, Awwad *et al.* (1986) observes a MD of 13.8% and 13.4% respectively. While, for benzene + $n\text{-C}_{10}$, the VW method predicts Lal *et al.* (2000) data with deviations of 12.6%, Awwad *et al.* (1986) is reproduced with a 13.4% MD. In general, data from Lal *et al.* (2000) is more accurately reproduced by the VW method due to the greater accuracy of the pure species viscosity. For more results the reader is referred to Table 7.

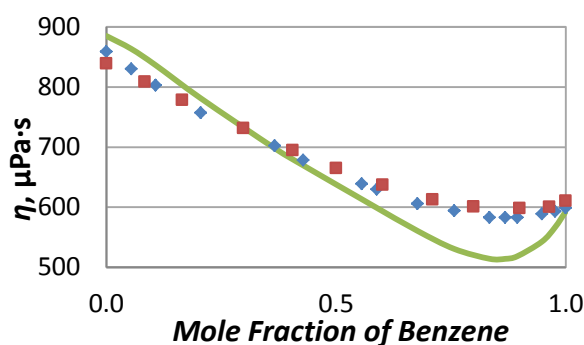


Figure 12 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with $n\text{-C}_{10}$. Experimental data: (♦) Lal *et al.* (2000), (■) Awwad *et al.* (1986). VW: (—)

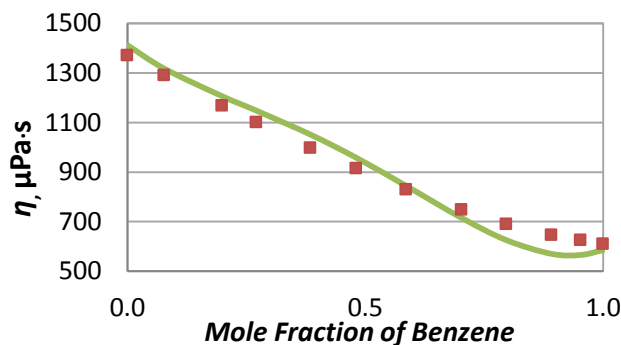


Figure 13 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with $n\text{-C}_{12}$. Experimental data: (■) Awwad *et al.* (1986). VW: (—)

Figure 14 shows that for the mixture of benzene + $n\text{-C}_{16}$, it was observed that the benzene correlation (Avgeri *et al.*, 2014) became negative at these densities. Therefore, at low benzene mole fraction the VW method did not produce results. Notwithstanding, at rich benzene condition Awwad *et al.* (1986) and Lal *et al.* (2000) was reproduced with MD 20.6% and 21.2%.

A general trend shown is the over prediction of mixture viscosity at low benzene mole fraction and the under prediction of mixture viscosity at rich benzene conditions. This can be explained through the understanding that parameter of pure species are calculated deeper into the 2-phase region where the benzene content becomes richer. Due to the lack of experimental data, the uncertainty within this region is greater. This brings additional uncertainty in the estimation of pure species parameters, therefore maximizing the deviation of the mixture viscosity.

These results indicate that for mixtures with aromatic molecules, VW model produces similar trends to experimental data, however further work on the VW model is required to increase the accuracy when the parameters of the pure species are computed in the 2-phase region.

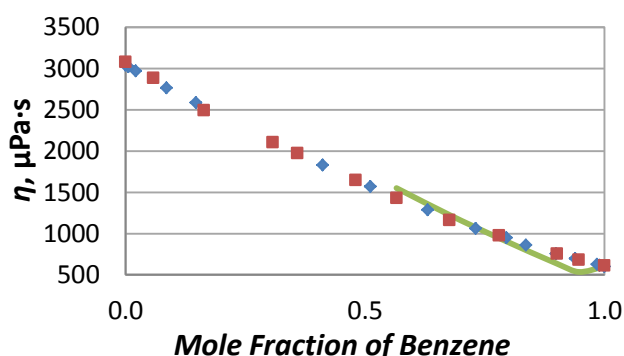


Figure 14 – Comparison between experimental viscosity data and calculated viscosity using VW method for mixtures of benzene with $n\text{-C}_{16}$. Experimental data: (♦) Lal *et al.* (2000), (■) Awwad *et al.* (1986). VW: (—)

Conclusion and Recommendation

A correlation of the dynamic viscosity of *p*-xylene was developed, through a critical assessment of the available experimental data. The correlation range of validity extends from (288 to 673) K up to 1100 bar. The correlation is expressed in terms of temperature and density, and the densities were obtained from the equation of state of Zhou *et al.* (2012). The correlation development focused around the interpolation of the 2-phase region. This was to ensure it is well-behaved when predicting this transition, where no experimental data is available. The correlation was tested against 11 primary authors with prediction uncertainty of 2.7%.

The application of the VW method for binary mixtures of benzene + *n*-C₆, *n*-C₈, *n*-C₁₀, *n*-C₁₂ or *n*-C₁₆ was studied. The estimation of the pure species parameter along with the effect of the mixing rule for χ_{ij} , and *n*-alkane reference correlation were explored. The VW method predicted mixture viscosities within 4% of the experimental data for mixtures with *n*-C₆. However, for the heavier *n*-alkanes deviations exceed 20%. This is believed to be due to the parameter of pure species being calculated deeper into the 2-phase region, where uncertainty is high as no experimental data is present. Overall the following conclusions can be made:

1. For binary mixtures of aromatic-alkane, pure species parameters should be estimated at equal reduced density
2. For *n*-alkane critical densities greater than aromatics, the VW model requires correlations for alkanes which have well-defined 2-phase region.
3. For the proposed viscosity correlation, behaviour at the 2-phase region makes it sufficient for developing a reference corresponding-states correlation for aromatic hydrocarbons or as part of the VW model to predict the viscosity of mixtures, containing *p*-xylene.

This paper furthers our understanding of the viscosity behaviour of mixtures with aromatic compounds. Therefore, several recommendations are put forward in order to enhance future work in this area. Accurate viscosity measurements of *p*-xylene are required at the supercritical region which ranged only up to 38 bar provided by one author, thus supercritical viscosity measurements at greater pressure ranges are required. Large pressure range experimental viscosity data within the vapour region and measurements along the vapour side of the saturation line are vital, as few authors provided data around these regions. These are essential in extending the experimental range of the correlation along with fortifying the current range. Subject to experimental data availability, this study could be extended to mixtures of *n*-alkanes and *p*-xylene to test the proposed correlation accuracy, in addition to widening the scope to more aromatic compounds. The critical density of *p*-xylene is lower than that of benzene; therefore better predictions from the VW method may be observed, as pure species parameters are calculated less deep in the 2-phase region. Lastly, further work on VW method for aromatic-alkane mixtures understanding effect of critical density on its predictive accuracy to further improve the model.

Nomenclature

B_η	= Second Viscosity Virial Coefficient	L/mol
MD	= Maximum Absolute Deviation	%
N_A	= Avogadro's Number	1/mol
<i>n</i> -C ₆	= <i>n</i> -Hexane	-
<i>n</i> -C ₈	= <i>n</i> -Octane	-
<i>n</i> -C ₁₀	= <i>n</i> -Decane	-
<i>n</i> -C ₁₂	= <i>n</i> -Dodecane	-
<i>n</i> -C ₁₆	= <i>n</i> -Hexadecane	-
P	= Pressure	bar
P_c	= Critical Pressure	bar
T	= Temperature	K
T_c	= Critical Temperature	K
T_r	= Reduced Temperature	-
V_{excl}	= Excluded Volume	-
$\alpha_i/\tilde{\alpha}_i$	= Measure of excluded volume of species <i>i</i> in the presence of species <i>i</i>	m ³ /mol
$\alpha_{ij}/\tilde{\alpha}_{ij}$	= Measure of excluded volume of species <i>i</i> in the presence of species <i>j</i>	m ³ /mol
$\Delta\eta$	= Residual Viscosity	μPa·s
ε/k	= Energy-Scaling Parameter	K
η	= Dynamic Viscosity	μPa·s
η^*	= Switch-over Viscosity	μPa·s
η_0	= Zero-density Viscosity Limit	μPa·s
η_1	= Initial-Density Coefficient	μPa·s·L/mol
η_{cal}	= Calculated Viscosity	μPa·s

η_{exp}	= Experimental Viscosity	$\mu\text{Pa}\cdot\text{s}$
$\eta_{0,ij}/\tilde{\eta}_{0,ij}$	= Mixture Interaction Viscosity in the Limit of Zero Density	-
η_{VW}	= Calculated Viscosity from the VW method	$\mu\text{Pa}\cdot\text{s}$
ρ^*	= Switch-over Density	mol/L
$\rho/\tilde{\rho}$	= Molar Density	mol/L
ρ_c	= Critical Density	mol/L
ρ_r	= Reduced Density	-
σ	= Size-Scaling Parameter	nm
$\chi_{0,ij}/\tilde{\chi}_{0,ij}$	= Radial Distribution Function at contact of species i in the presence of species j in the limit of zero density	-
$\chi_i/\tilde{\chi}_i$	= Radial Distribution Function at contact of species i in the presence of species i	-
$\chi_{ij}/\tilde{\chi}_{ij}$	= Radial Distribution Function at contact of species i in the presence of species j	-

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Appendix

Appendix A – Critical Literature Review

Table A1 – Milestones in Prediction of Viscosity of Dense Mixtures

References	Year	Title	Authors	Contribution
Swedish Academic Proceedings (Svensk. Akad. Handl.), Vol. 63, No. 4	1922	Kinetic Theory of Thermal Conduction Viscosity and Self-Diffusion in Certain Dense Gases and Liquids	Enskog, D.	Proposed an approximation of the kinetic theory for rigid sphere dense gases.
Phys. A Stat. Mech. its Appl., Vol. 95, No. 3, p.602–608	1979	On the Viscosity and Thermal Conductivity of Dense Gases	Sandler, S.I., Fiszdon, J.K.	Introduction of the switch-over point concept to obtain values of the radial distribution function for pure species over a range of densities
Int. J. Thermophys., Vol. 44, No. 10, p2181–2189	1989	Prediction of the Viscosity of Fluid Mixtures Over Wide Ranges of Temperature and Pressure	Vesovic, V., Wakeham, W.A.	Extended the Thorne-Enskog equations for the prediction of the viscosity of high-density fluid mixture (VW spheres)
Fluid Phase Equilib., Vol. 79, p313–326	1992	Vapor Phase Viscosity of Toluene and <i>p</i> -Xylene	Vogel, E., Hendl, S.	Only experimental data with extensive data on zero-density and initial density dependence viscosity
Int. J. Thermophys., Vol. 13, No. 5, p895–905	1992	Correlation and Prediction of Dense Fluid Transport Coefficients. V. Aromatic Hydrocarbons	Assael, M. J., Dymond, J. H., Patterson, P. M.	Provides theoretical guidance in developing the empirical form of the residual viscosity using the hard-sphere model. Incorporation of the shape factor accounting for non-sphericity of hydrocarbons with carbon number greater than 1
2 nd Edition, New York, Cambridge University Press	2005	Transport Properties of Fluids: Their Correlation Prediction and Estimation	Millat, J., Dymond, J.H., Nieto de Castro, C.A.	Correlation techniques with theoretical background of various transport properties such as viscosity
J. Chem. Phys., Vol. 128, No. 20, p204901	2008	A Kinetic Theory Description of the Viscosity of Dense Fluids Consisting of Chain Molecules.	de Wijn, A.S., Vesovic, V., Jackson, G., Trusler, J.P.M.	Extended the modified Enskog theory to represent long molecules as chains of rigid spheres
J. Chem. Phys., Vol. 136, No. 7, p074514	2012	Viscosity of Liquid Mixtures: The Vesovic-Wakeham Method for Chain Molecules.	de Wijn, A.S., Riesco, N., Jackson, G., Trusler, J.P.M., Vesovic, V.	Extended the scheme given by de Wijn <i>et al.</i> (2008) to model viscosity of liquid mixtures consisting of VW-chains

Swedish Academic Proceedings (Svensk. Akad. Handl.) 63 (4) (1922)

“Kinetic Theory of Thermal Conduction Viscosity and Self-Diffusion in Certain Dense Gases and Liquids”

Authors: Enskog, D.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Proposed an approximation of the kinetic theory for rigid sphere dense gases.

Objective:

To extend the kinetic theory to dense gases

Methodology Used:

The Boltzmann equation for a dilute gas of rigid spheres was generalized to dense gases. The difference in position of the colliding hard spheres and the increase in the frequency of collisions were accounted for by χ . This factor, χ , defines the radial distribution function at contact of fluid in thermal equilibrium.

Conclusion:

The Boltzmann equation for a dilute gas of rigid spheres can be used to predict viscosity of the dense gas rigid sphere.

Comments:

***Phys. A Stat. Mech. its Appl.* 95 (3) (1979) 602–608**

“On the Viscosity and Thermal Conductivity of Dense Gases”

Authors: Sandler, S.I. and Fiszdon, J.K.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Introduction of the switchover point concept to obtain values of the radial distribution function for pure species over a range of densities

Objective:

Utilising measured transport property data, information on χ is extracted to elude observation of unphysical behaviour

Methodology Used:

Experimental data is used to acquire the effective size parameter for molecules in place of thermodynamic data. With this scheme, a switch-over point is defined where the solution of the inverted Enskog's equation for density dependence of viscosity is switched from negative to positive root.

Conclusion:

Applying the switch-over point, physically reliable behaviour of the radial distribution function could be attained.

Comments:

***Int. J. Thermophys.* 10 (1) (1989) 125–132**

“Prediction of the Viscosity of Fluid Mixtures Over Wide Ranges of Temperature and Pressure”

Authors: Vesovic, V. and Wakeham, W.A.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Extended the Thorne-Enskog equations and the concept of switch-over point for the prediction of mixture viscosity (VW-spheres)

Objective:

The development of a reliable method for the prediction of dense gas mixture viscosity.

Methodology Used:

Transport data was used to estimate pure species parameters. The switch-over point scheme was used to obtain physically reliable pseudo radial distribution function. Mixing rules based on both Lebowitz's solution of the Percus-Yevick equation (LPY equation) and on the Carnahan-Starling equation was proposed for the calculation of χ_{ij} .

Conclusion:

The use of switch-over point to obtain the pseudo radial distribution function allows this method to apply to very high densities. The scheme was tested on mixtures of natural gas, with viscosity predictions within the claimed uncertainty of the experimental data.

Comments:

This scheme was tested further on high density mixtures in a subsequent paper; *Chem. Eng. Sci.* **44** (10) (1989) 2181–2189

***Fluid Phase Equilib.* 79 (1992) 313–326**

“Vapour Phase Viscosity of Toluene and *p*-Xylene”

Authors: Vogel,E. and Hendl,S.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Only experimental data with extensive data on zero-density and initial density dependence viscosity

Objective:

Reported new measurements of the vapour phase viscosity of toluene and *p*-xylene

Methodology Used:

Measurements have been performed in an all-quartz oscillating-disk viscometer with small gaps. The temperature range between (305 to 630) K (toluene) and between (340 to 635) K (*p*-xylene) and for densities from (0.002 to 0.045) mol/L (toluene) and from (0.003 to 0.038) mol/L (*p*-xylene). The data was evaluated with a density series for the viscosity in which only a linear density contribution has been included.

Conclusion:

The values of the second viscosity virial coefficient obtained for toluene and *p*-xylene have been compared with results of the Rainwater-Friend theory on the basis of the Lennard-Jones 12-6 potential with good agreement.

Comments:

***Int. J. Thermophys.* 13 (5) (1992) 895–905**

“Correlation and Prediction of Dense Fluid Transport Coefficients. V. Aromatic Hydrocarbons”

Authors: Assael, M. J., Dymond, J. H. and Patterson, P. M.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Provides theoretical guidance in developing the empirical form of the residual viscosity using the hard-sphere model. Proposed reference viscosity correlations for *n*-alkanes with well-defined 2-phase regions. The incorporation of the shape factor accounting for non-sphericity of hydrocarbons with carbon number greater than 1.

Objective:

To show that the proposed scheme based upon rigid-sphere theory can be combined with the universal equation relating viscosity to reduced volume in order to accurately predict the viscosity of aromatic hydrocarbons over wide ranges of temperature and pressure and at densities greater than the critical density.

Methodology Used:

Previously derived relationships combined with laboratory measurements of viscosity of benzene, toluene, and the three forms of xylene and literature values for those and other aromatics. Used the lab data to parameterize the relationship for reduced volume of aromatics based upon carbon number and temperature.

Conclusion:

Agreement is excellent with only 3% of data points deviating from lab measurements by more than 5%.

Comments:

Further testing of the scheme was presented in a subsequent paper; *Int. J. Thermophys.* **30 (6)** (2009) 1733–1747

2nd ed., New York, Cambridge University Press (2005)

“Transport Properties of Fluids: Their Correlation Prediction and Estimation”

Authors: Millat, J., Dymond, J.H. and Nieto de Castro, C.A.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Correlation techniques with theoretical background of various transport properties such as viscosity

Objective:

Describes the methods and application for evaluating the transport properties, such as viscosity, thermal conductivity and diffusion, of pure gases and fluid mixtures.

Methodology Used:

Case studies of transport property analysis for real fluids are made, with a discussion of various international data banks and prediction packages.

Conclusion:

Pure species viscosity can be predicted using kinetic theory and various data banks

Comments:

***J. Chem. Phys.* 128 (20) (2008) 204901**

“A Kinetic Theory Description of the Viscosity of Dense Fluids Consisting of Chain Molecules”

Authors: de Wijn, A.S., Vesovic, V., Jackson, G. and Trusler, J.P.M.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Extended the modified Enskog's theory to represent long molecules as chains of rigid spheres

Objective:

Propose a theoretical model for the viscosity of chained molecules

Methodology Used:

Molecules are approximated by chains of equal-sized, tangentially jointed, rigid spheres (segments). Based on Enskog's theory, the viscosity equation was modified to include excluded volume, density, zero-density limit viscosity and the radial distribution function for segments. Excluded volume was defined in terms of two molecular parameters, the diameter of the spherical segment and the number of segments in a chain. Segment size is analogous to a methane molecule at that temperature.

Conclusion:

This extended scheme improves the predictive capabilities of the model. The chain length becomes independent of temperature by incorporating the effect of temperature on segment size.

Comments:

***J. Chem. Phys.* 136 (7) (2012) 074514**

“Viscosity of Liquid Mixtures: The Vesovic-Wakeham Method for Chain Molecules.”

Authors: de Wijn, A.S., Riesco, N., Jackson, G., Trusler, J.P.M. and Vesovic, V.

Contribution to the Prediction of Viscosity of Dense Mixtures:

Extended the scheme given by de Wijn *et al.* (2008) to model viscosity of liquid mixtures consisting of VW-chains

Objective:

Propose a theoretical model for the viscosity of a chain-fluid mixture. Like presented in de Wijn *et al.* (2008) evaluation of different effective parameters is required for a chain-like fluid mixture. To then, illustrate the predictive capabilities of the VW chain model.

Methodology Used:

Utilised SAFT-type analysis and extended the mixing rules for mixture interaction parameters presented in the original VW method for segment fluid.

Conclusion:

Pure species properties should be estimated as the same reduced density as the mixture. To accurately reproduce the experimental viscosity, different effective sizes of molecules should be used for the excluded volume (σ_a) and collision dynamics (σ_χ).

Comments:

Appendix B – Miscellaneous Results for the Empirical Correlation for *p*-XyleneTable B1 – Data Used In Developing the Viscosity Correlation of *p*-Xylene

Authors	Year Publ.	Technique Employed	Purity (%)	No. of Data	Temperature Range (K)	Pressure Range (bar)
Primary Data						
Mamedov and Panchenkov	1955	C	99	7	293 – 353	1
Mamedov <i>et al.</i>	1968	C	99.78	129	323 – 548	1 – 400
Nissema and Koskenniska	1972	C	-	4	293 – 323	1
Mamedov <i>et al.</i>	1975	C	99.4	124	323 – 548	1 – 400
Kashiwagi and Makita	1982	TC	99	60	298 – 348	1 – 1094
Abdullaev and Akhundov	1983	C	-	27	473 – 673	1 – 38
Dymond and Robertson	1985	C	99	6	298 – 393	P _{Sat}
Serrano <i>et al.</i>	1990	C	99.98	4	288 – 303	1
Vogel and Hendl	1992	C	99.9	66	383 – 633	0.08 – 2
Et-Tahir <i>et al.</i>	1995	FB	99	12	313 – 353	200 – 1000
Exarchos <i>et al.</i>	1995	C	99.5	5	293 – 313	1
Secondary Data						
Schmack <i>et al.</i>	1973	C	-	3	293 - 323	1
Chevalier <i>et al.</i>	1990	C	99.95	1	298	1
Wanchoo and Narayan	1992	C	-	4	293 - 318	1
Petrino <i>et al.</i>	1995	C	99.5	1	298	1
Wankhede <i>et al.</i>	2008	C	99	3	288 - 308	1
Dominguez-Perez <i>et al.</i>	2009	C	99	1	298	1
Habibullah <i>et al.</i>	2010	C	99	3	303 - 323	1
Ikeuchi <i>et al.</i>	2010	C	99.8	6	288 - 313	1

C – Capillary; FB – Falling Body; RB – Rolling Body; TC – Torsional Crystal

Appendix C – Miscellaneous Results for VW Method for Mixtures

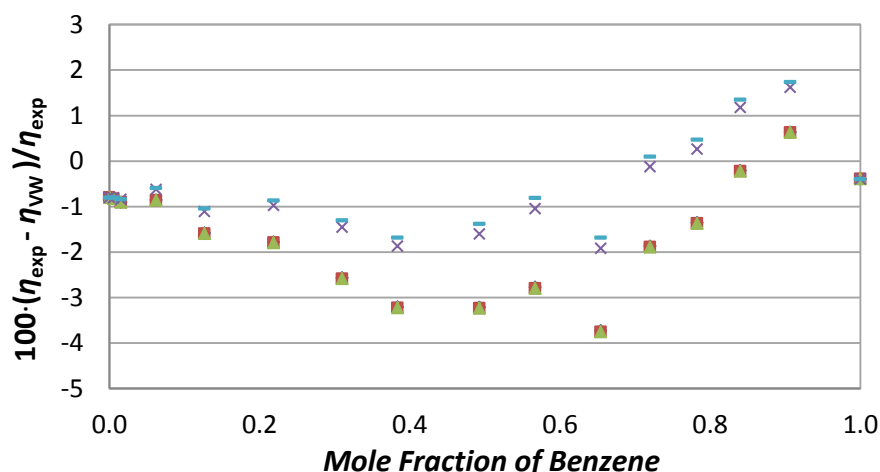


Figure C1 – Percentage deviation $[100 (\eta_{exp} - \eta_{VW}) / \eta_{exp}]$ between experimental viscosity of Lal *et al.* (2000) and calculated viscosity using VW method for different mixing rules for χ_{ij} for a mixture of benzene with n -C₆. (♦) Ansatz#1, (■) Ansatz#2, (▲) Ansatz#3, (×) Ansatz#4, (–) Ansatz#5

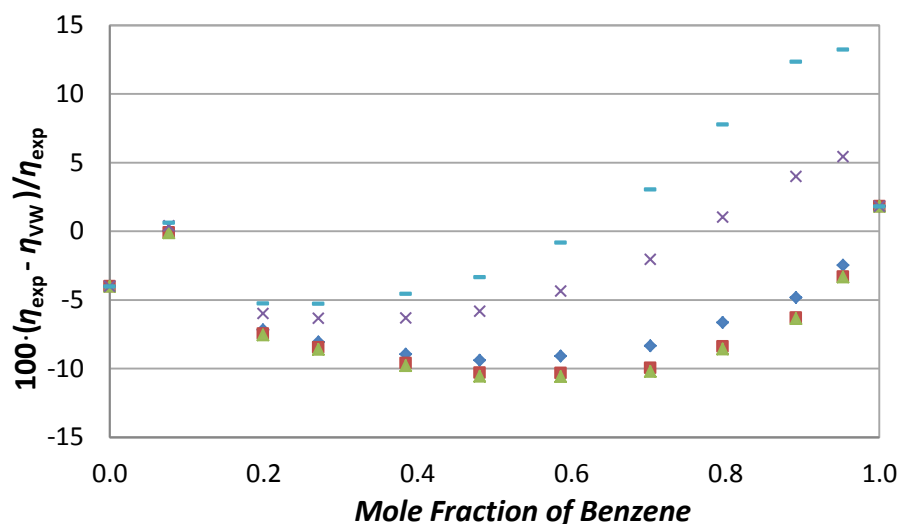


Figure C2 – Percentage deviation $[100 (\eta_{exp} - \eta_{VW}) / \eta_{exp}]$ between experimental viscosity of Awwad *et al.* (1986) and calculated viscosity using VW method for different mixing rules for χ_{ij} for a mixture of benzene with n -C₁₂. (♦) Ansatz#1, (■) Ansatz#2, (▲) Ansatz#3, (×) Ansatz#4, (–) Ansatz#5

The effect of using different mixing rules proposed by de Wijn *et al.* (2012) was studied. The results are presented in Figure C1 and Figure C2. It was reported by de Wijn *et al.* (2012) and Tariq (2013) that while there are variances in prediction for different mixing rules, the overall trend was to shift the deviations, but not affect the trend in mole fraction.

The same observation was seen in this study with benzene + n -C₆ or n -C₁₂. The mixing rules 4-5 were consistently higher than 1-3. For lighter mixtures, n -C₆, mixing rules 4-5 exhibit lower deviations while for heavier mixtures, n -C₁₂, mixing rules 1-3 exhibit lower deviations. It can be therefore concluded that chain length can affect the predictions of the VW method, with aromatic molecules, using different mixing rules. This was also observed by de Wijn *et al.* (2012) and Tariq (2013) for mixtures with n -alkane and cyclic molecules, respectively. Both authors recommended further investigation in this area to develop theoretical connection between the mixture species and mixing rule used.

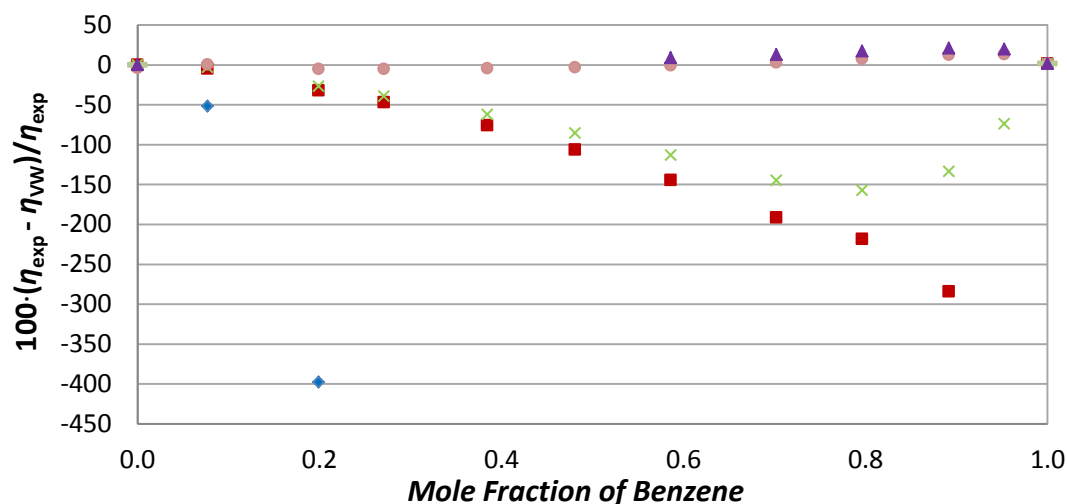


Figure C3 – Percentage deviations $[100(\eta_{exp} - \eta_{VW})/\eta_{exp}]$ of different pure species conditions on the VW method predictive capabilities for the mixture of benzene with $n\text{-C}_{12}$ of Awwad *et al.* (1986). (♦) Equal molar density, (■) Equal segment density, (×) Equal mass density, (●) Equal reduced density, (▲) Equal reduced density and temperature

Figure C3 shows the effect of altering the density choice on a benzene + $n\text{-C}_{12}$ mixture from Awwad *et al.* (1986). Equal reduced density reproduced the data with a maximum error of 13.2%, whereas, with the other options errors ranging from 20% to 400 % were realized. For mixtures with heavier n -alkanes it can be concluded that equal reduced density should be used. The reason deviation is outside the experimental accuracy is possibly due to the uncertainty within the calculations of the pure species within the 2-phase region. To avoid this in future, it is recommended to ensure that reference correlations used for the VW method, have well-defined 2-phase regions.