

HYDROGEN SULPHIDE VISCOSITY MODELLING

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ABSTRACT

As regulations for emissions of carbon dioxide and hydrogen sulphide into the atmosphere are becoming stricter and the penalty for violation increases, new and economical ways of reducing these emissions are becoming increasingly important to everyday operations. One promising sequestering option is the injection of acid gas mixtures into formations for disposal/storage. During the design of these acid gas injection schemes a comprehensive knowledge of the thermo-physical properties is of utmost importance in determining the feasibility and size of these operations.

Recently, the friction theory (f-theory) for viscosity modelling has been shown to accurately determine the viscosity behaviour of a wide range of petroleum fluid systems ranging from natural gases to heavy crude oils. This technique has also been shown to accurately model mixtures containing various concentrations of CO₂. However, in the development of the f-theory hydrogen sulphide was not explicitly studied and therefore needs to be accounted for to ensure it is accurately modelled.

The development/validation of any modelling approach requires a thorough knowledge of the available data. With this in mind, an exhaustive review of the data available in the literature has been performed revealing a very limited number of experimental points available in the open literature for the viscosity of pure H₂S and H₂S mixtures. In this investigation, the applicability of the f-theory for viscosity modelling will be tested to reproduce the existing experimental viscosities of hydrogen sulphide and its mixtures.

HYDROGEN SULPHIDE VISCOSITY MODELLING

INTRODUCTION

Acid gas injection (AGI) is a widely used process for the disposal of mixtures of hydrogen sulphide and carbon dioxide. The acid gas is the by-product of the sweetening process, which is used to remove the H₂S and CO₂ from raw natural gas.

Typically these AGI schemes are small scale (less than 5 MMSCFD or 140x10³ Sm³/d) and are for the disposal of the gas mixture. However some have used the acid gas as a miscible flood fluid or for pressure maintenance. In addition larger producers are considering acid gas injection as an option to the production of elemental sulphur.

Although basically the same, when compared to traditional schemes these large injection schemes pose some new problems. In the small injection schemes the pressure drop due to fluid flow in both the acid gas pipeline and the injection well are negligibly small. Thus it is not necessary to have accurate prediction of the viscosity. However for the large injection schemes the selection of the optimum pipeline and well diameter requires a more accurate calculation of the viscosity.

Accurate viscosity data are also useful for the estimation of the injection pressure. The viscosity is a key parameter for modelling the flow of the fluid through the reservoir. Fortunately there is a plethora of data for the viscosity of carbon dioxide, which are useful for model building and testing. On the other hand, there is a dearth of data for the viscosity of hydrogen sulphide. Even worse, some of the available are not accurate enough – even for engineering purposes.

LITERATURE REVIEW

As accurate modelling techniques are data driven, the development of these models requires a thorough knowledge of existing literature data and the acquisition of new experimental measurements to fill the void of the existing data sets. There are few data for the viscosity of hydrogen sulphide and these data are scattered throughout the open literature and a complete databank containing a critical analysis of the published results has not been fully developed yet. Such a compilation is necessary to model development and will certainly benefit scientists and engineers working in this field. It is important to identify where additional data are needed to fill voids, resolve discrepancies of existing data sets and to extend regions where the physical properties (e.g. viscosity) are insufficiently modelled with the current techniques.

A comprehensive literature review revealed relatively few investigations into viscosity of hydrogen sulphide. A complete list of the data sets used in this investigation is presented in Table I indicating a limited number of the corresponding existing data sets; the bulk of the data to gaseous H₂S at 1.013 bar. The remainder of the data is scattered throughout the H₂S *T-η-P* surface with no consistent effort to fill the voids left by previous investigations. Most of the work was performed in the 1960s and 1970s after which no further work into this area appears to have been carried out.

Table I. Experimental Investigations of the Viscosity of Hydrogen Sulphide

Investigators	Year	Reference
Graham	1846	[1]
Steele, McIntosh & Archibald	1904, 1906	[2-4]
Rankine & Smith	1921	[5]
Jung & Schmick	1930	[6]
Hennel & Krynicki	1959	[7]
Pal & Barua	1967	[8]
Monteil, Lazarre, Salvinien & Viallet	1969	[9]
Pal & Bhattacharya	1969	[10]
Bhattacharya, Ghosh & Barua	1970	[11]
Bhattacharya	1970	[12]
Runnovskaya, Zorin & Devyatikh	1970	[13]

After a robust examination of the all the data, the data sets of Steele et al. [2-4] and Monteil et al. [9] were not considered in the development of a reference H₂S viscosity f-theory model and the subsequent development of the one parameter form of the f-theory. These data exhibited inconsistencies with the rest of the data set, results from Molecular dynamics simulation [14], with corresponding states reasoning with carbon dioxide and ethane [15] and with previous critical reviews into the groups equipment, measurements and accuracy [16,17]. Additionally, Monteil et al. [9] stated that the results cannot be used for theoretical treatment. Molecular dynamic simulation [14] supports the results from Runnovskaya et al. [13] and confirms the rejection of the data from Steele et al. [2-4]. Similarly, comparisons with the T - η - P surfaces of carbon dioxide and ethane also confirm the rejection of the data from Steele et al..

THE FRICTION THEORY

The friction theory or f-theory for viscosity modelling has been developed based on friction concepts of classical mechanics and the van der Waals theory of fluids. The theory was originally developed on the basis that the van der Waals repulsive and attractive pressure terms, which can be obtained from simple cubic equation of states, could be connected to the Amonton-Coulomb friction law. This connection results in a residual viscosity term that is added to the dilute gas viscosity term to estimate the viscosity of fluids over a wide range of temperature and pressure conditions. As a result, this model has been shown to be widely versatile and accurate in the correlation and prediction of the viscosity of well-defined pure, binary and multi-component systems [15,18-23] and even complex reservoir fluid systems ranging from natural gases to heavy crude oils [24-28].

The f-theory was originally applied to several widely used cubic EoS of the van der Waals type, such as the Soave-Redlich-Kwong (SRK) EoS [29] or the Peng-Robinson (PR) EoS [30], as well as to the PC-SAFT EoS [31-33], a non-cubic EoS consisting of separate repulsion and attraction terms. In a recent work [15], however, the restriction of having to use an EoS constructed on an explicit separation between attractive and repulsive terms has been removed allowing the application of the f-theory to practically all type of EoS. This has lead to the possibility of using highly accurate reference type EoS resulting also in highly accurate reference quality viscosity models. Consequently, the f-theory models presented in this work consist of two levels: level 1 relates to the development of a reference type f-theory model for H₂S as accurate as the available data and extended knowledge

allows. Level 2 consists in using the developed reference model as a base for the derivation of the required scaling parameters to be used in the one-parameter f-theory model [22], which is the basic model that has been extensively applied to the accurate description of reservoir fluids.

The H₂S f-theory Reference Model

According to the f-theory for viscosity modelling, the viscosity of a fluid can be separated into a dilute gas term, η_0 , and a residual friction term, η_f .

$$\eta = \eta_0 + \eta_f \quad (1)$$

According to the kinetic theory by Chapman and Engskog [34], the dilute gas limit, η_0 , is due to the particle kinematics, is only temperature dependent and it is most relevant for the gas phase. In previous f-theory related works the semi-empirical predictive model by Chung et al. [35] which delivers a reasonable absolute average deviation (AAD) of around 1.5% for non-polar compounds, has been extensively used for the calculation of η_0 . However, in the derivation of the H₂S viscosity reference model a simple yet accurate empirical equation for η_0 similar to ones used in [15], will be also used in this work:

$$\eta_0 = d_0 + d_1 T_r^{1/4} + d_2 T_r^{1/2} + d_3 T_r^{3/4} \quad (2)$$

where T_r is the reduced temperature ($T_r = T/T_c$). The values of the coefficients in equation (2) have been obtained by regressing all of the available low-pressure H₂S data in combination with a first order f-theory model. However, the raw data accuracy does not allow for a high accuracy in the dilute gas model and therefore the best derived results corresponds to values for the coefficients of $d_0 = 436.694$, $d_1 = -1215.30$, $d_2 = 935.279$ and $d_3 = 0$, with units of μP - the model accuracy is only of around 1.25% for the dilute gas limit.

For the derivation of the friction theory, the quadratic general f-theory model proposed in [15],

$$\eta = \eta_0 + \kappa_i P_{id} + \kappa_r \Delta P_r + \kappa_a \Delta P_a + \kappa_i P_{id}^2 + \kappa_{rr} \Delta P_{rr}^2 + \kappa_{aa} \Delta P_a^2 \quad (3)$$

has been used in combination with the H₂S coefficients recently published by Lemmon and Span [36] for the short Span-Wagner EoS. According to the generalization f-theory work by Quiñones-Cisneros and Deiters [15], the pressure terms in equation (3) are related to the internal pressure (π_T) according to the following equations:

$$P_r = T \left(\frac{\partial P}{\partial T} \right)_v \quad (4)$$

$$P_a = P - P_r = -\pi_T \quad (5)$$

and

$$P_r = P_{id} + \Delta P_r \quad (6)$$

where ΔP_r is a residual of the repulsive term after subtracting the ideal pressure term from P_r .

The model given by equation (3) is highly accurate but also sensitive and requires a good dataset to be regressed against for optimal performance. In the case of H₂S this is a major limitation, as shown in the previous section, with the exception of some coexistence liquid and low-pressure vapour data there are no reliable H₂S viscosity measurements.

Therefore, in order to develop a reasonable model to be used as a reference H₂S model, the available data has been complemented with scaled data from fluids that “arguably” may show a similar qualitative performance as H₂S. In the case of the low-density region, polarity is most relevant as it may induce a flat, or even decreasing, initial density dependency. This is a phenomenon shown by polar substances, H₂S is slightly polar and it is likely to have a viscosity initial density behaviour qualitatively similar to CO₂, a fluid for which extensive reliable data is available. On the other hand, for a simple not too polar substance such as H₂S the dense phase viscosity performance is most sensitive to molecular structure. For practical purposes, molecular structure of simple molecules may somehow be described by the acentric factor and this may imply a high-pressure performance of H₂S that qualitatively resembles that of ethane, a fluid with an acentric factor close to the one of H₂S and for which there are also extensive reliable data.

As such, this work H₂S reference model has been developed by combining the available reliable H₂S data with low pressure scaled CO₂ data and elevated pressure scaled ethane (C₂H₆) data. The EoS used here are classical ones, i.e. of an analytical nature that do not necessarily show any sort of critical divergence, and therefore a convenient scaling parameter is the estimated viscosity at the critical point. Thus, the model derivation was carried out by iteratively scaling up the CO₂ and the ethane reduced data using the resulting H₂S viscosity value estimated at the critical point until a reasonable agreement and performance was arguably achieved.

Clearly, the procedure above described can be a subject of criticism but it can also be argued that, given the extent of experimental information available, is the best that can be done under the circumstances. Thus, for the final correlation, the temperature dependencies of the friction constants in equation (3) are given by [15]:

$$\kappa_a = (a_0 + a_1\psi_1 + a_2\psi_2)\Gamma \quad (7)$$

$$\kappa_{aa} = (A_0 + A_1\psi_1 + A_2\psi_2)\Gamma^3 \quad (8)$$

$$\kappa_r = (b_0 + b_1\psi_1 + b_2\psi_2)\Gamma \quad (9)$$

$$\kappa_{rr} = (B_0 + B_1\psi_1 + B_2\psi_2)\Gamma^3 \quad (10)$$

$$\kappa_i = (c_0 + c_1\psi_1 + c_2f(\Gamma))\Gamma \quad (11)$$

$$\kappa_{ii} = (C_0 + C_1\psi_1 + C_2\psi_2)\Gamma^3 \quad (12)$$

where

$$\psi_1 = \exp(\Gamma) - 1 \quad (13)$$

$$\psi_2 = \exp(\Gamma^2) - 1 \quad (14)$$

$$\Gamma = \frac{T_c}{T} \quad (15)$$

Against the considered extended database the model delivers an absolute average percentage deviation (*AAPD*) of only 1.06% with a negligible bias of just 0.03%, indicating a well balanced performance between the low density and the dense phases.

The resulting f-theory parameters for the correlation to go with the H₂S f-theory reference model coupled with the H₂S Lemmon-Span [36] short form of the Span-Wagner EoS are reported in Table II.

Table II. Hydrogen Sulphide Reference Friction Theory Model Parameters

Parameter	($\mu\text{P}/\text{bar}$)
a_0	5.46919×10^{-1}
a_1	-7.32295×10^{-2}
a_2	-7.35622×10^{-2}
b_0	4.56159×10^{-1}
b_1	-1.82572×10^{-1}
b_2	-6.59654×10^{-2}
c_0	-4.33882×10^{-2}
c_1	6.13716×10^{-2}
c_2	0
	($\mu\text{P}/\text{bar}^2$)
A_0	6.67324×10^{-5}
A_1	-2.16365×10^{-5}
A_2	0
B_0	-1.53973×10^{-5}
B_1	2.17652×10^{-5}
B_2	0
C_0	3.54228×10^{-3}
C_1	-4.76258×10^{-4}
C_2	0
ΔT (K)	190-600
Max. P (bar)	1000
AAPD	1.06 %
Bias	0.03 %

The overall model performance is also depicted in Figure 1 where the co-existing phase viscosity and some selected isobars are shown. The points in Figure 1 represent the co-existing experimental data for the liquid phase and the low pressure data (around 1 bar) for the vapour phase.

Figure 2 shows this work's model in comparison with the available experimental data and the results from the H₂S model in the NIST package of thermo-physical properties REFPROP [37,38], which can be considered a reference in the field.

Clearly, the results obtained with the approach followed in this work appear to be of higher accuracy. Yet, this must be taken with caution as at high pressures, such as 1000 bar, deviations up to 10 % could be possible. This accuracy issue can only be addressed through further experimental work.

The H₂S One Parameter f-theory Model

The further development of the H₂S necessary scaling parameters to go into the one-parameter f-theory models [22] is of relevance as such models have been shown to be capable of accurately describe the viscosity of a wide variety of reservoir fluids under broad conditions [27]. For that purpose, the general f-theory model described above has been used as reference for the tuning of the one-parameter model. A detailed description of the f-theory one parameter viscosity modelling procedure is readily available [22] and only a brief summary will be given here.

For reservoir fluids applications the model of Chung et al. [35] provides sufficient accuracy and is recommended for the viscosity prediction of the dilute gas term.

$$\eta_o = 40.785 \frac{\sqrt{MWT}}{v_c^{2/3} \Omega^*} F_c \quad (16)$$

where the following empirical equation is used to estimate the reduced collision integral

$$\Omega^* = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \times 10^{-4} T^{*0.14874} \sin(18.0323T^{*-0.76830} - 7.27371) \quad (17)$$

with

$$T^* = \frac{1.2593T}{T_c} \quad (18)$$

The F_c factor was empirically found to be:

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \quad (19)$$

here μ_r is a dimensionless dipole moment and κ is a hydrogen bonding correction factor. When non-polar compounds are considered equation (19) reduces to:

$$F_c = 1 - 0.2756\omega \quad (20)$$

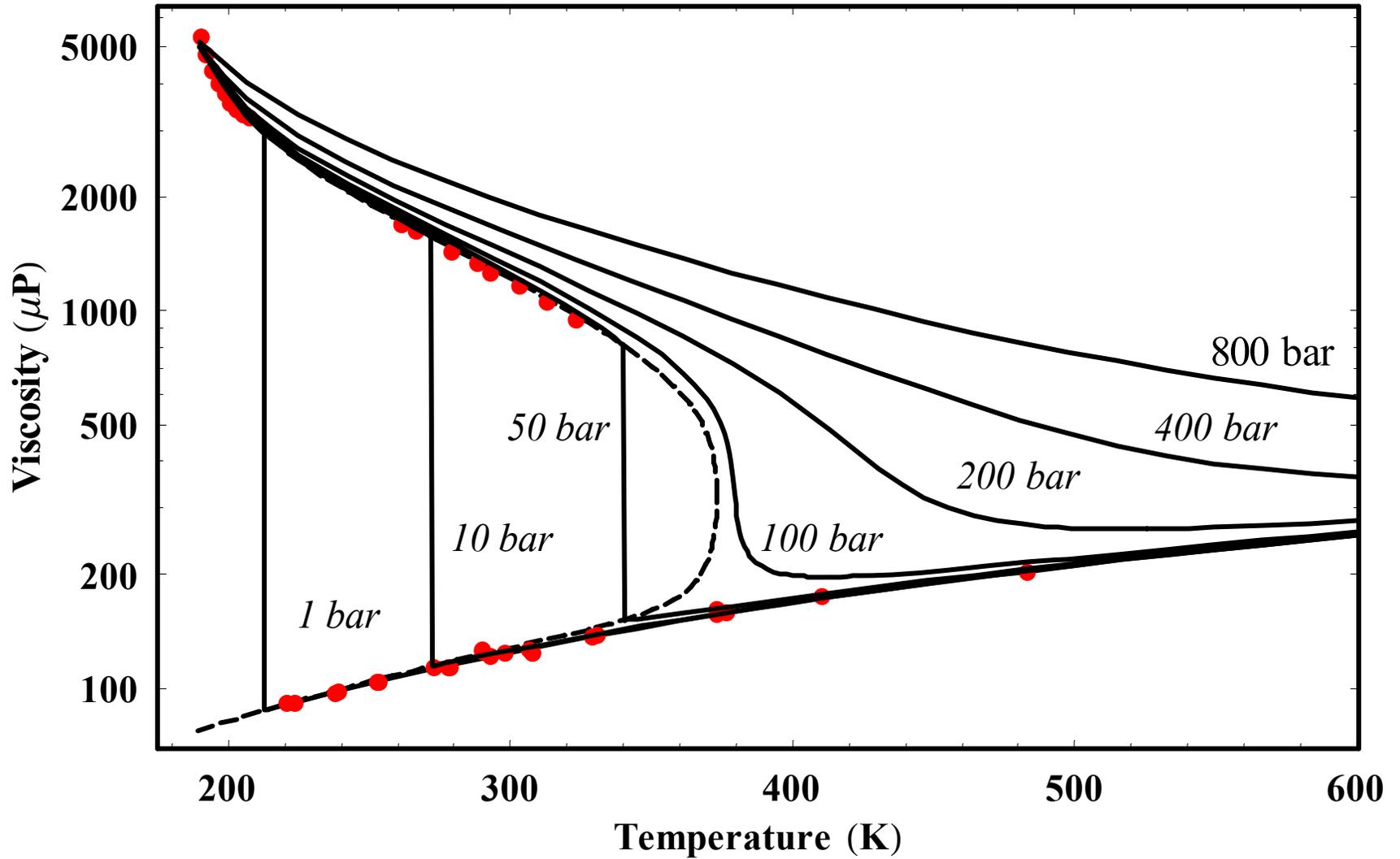


Figure 1. Reference H₂S viscosity model performance along with liquid coexistence and low pressure data (corresponding to pressures close to 1 bar). Solid lines: isobaric curves; Dashed lines: equilibrium phase curves.

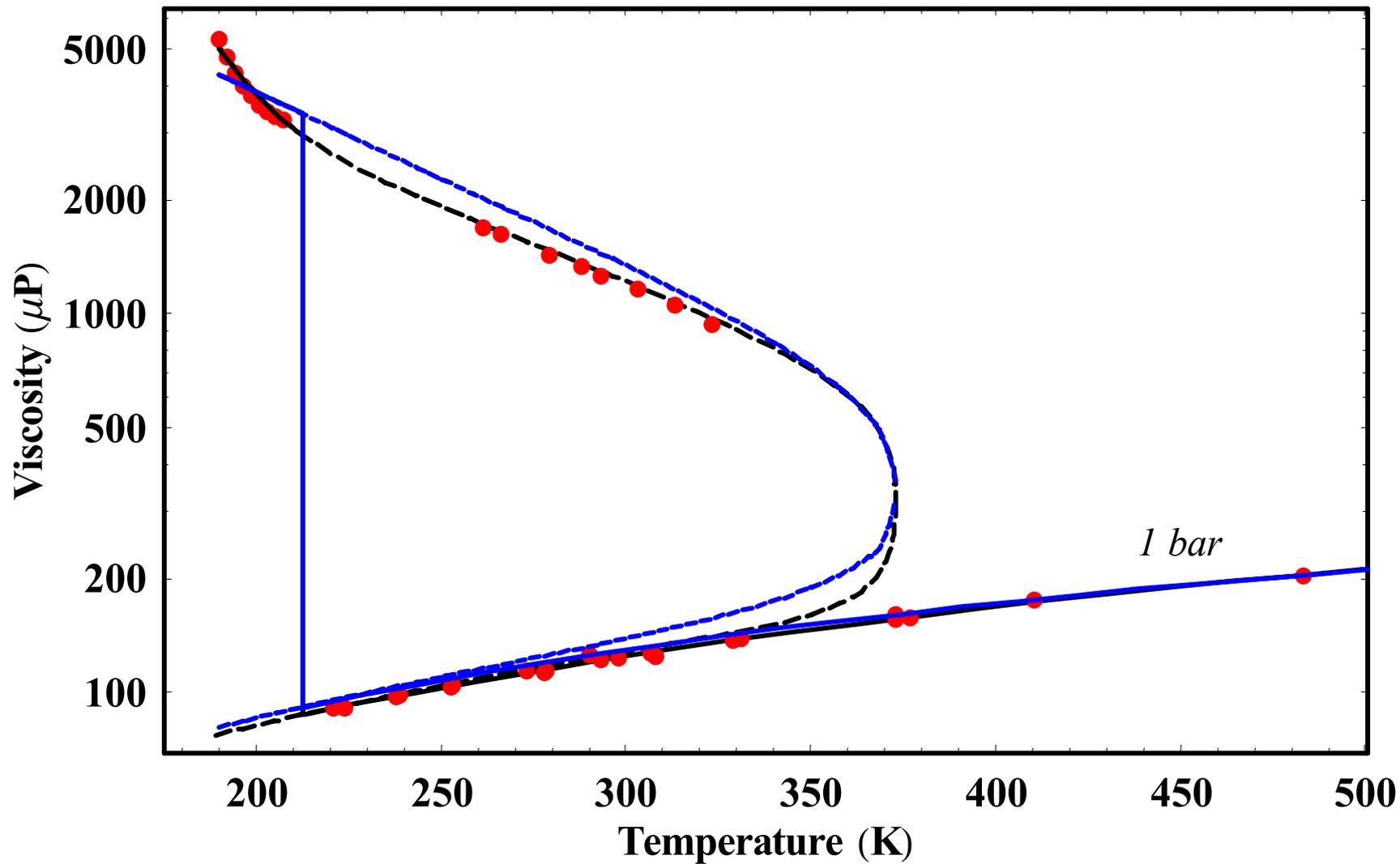


Figure 2. Reference H₂S viscosity model performance together with the model implemented in the NIST REFPROP package. Points: coexisting liquid and low pressure data (corresponding to pressures close to 1 bar). Solid lines: 1 bar isobar; Dashed lines: equilibrium phase curves.

For components without tabulated values of the critical volume, v_c , can be obtained from the expression in Quiñones-Cisneros et al. [24], which gives reasonable results for reservoir fluids applications.

The expression for the residual friction term in the one-parameter model is:

$$\eta_f = \hat{\eta}_f \eta_c \quad (21)$$

where η_c represents the “one” characteristic viscosity scaling parameter and in the case of cubic EoS corresponds to the “classical” viscosity evaluated at the critical point (this as opposed to an actual plausible critical viscosity divergence that may result from renormalized EoS).

The reduced friction term is made up of a contribution of a reduced repulsive and attractive contribution.

$$\hat{\eta}_f = \hat{\eta}_{f,r} + \hat{\eta}_{f,a} \quad (22)$$

where the attractive term is given by:

$$\hat{\eta}_{f,a} = \hat{\kappa}_a \left(\frac{P_a}{P_c} \right) \quad (23)$$

and the reduced term is given by:

$$\hat{\eta}_{f,r} = \hat{\kappa}_r \left(\frac{P_r}{P_c} \right) + \hat{\kappa}_{rr} \left(\frac{P_r}{P_c} \right)^2 \quad (24)$$

Here, P has been used to emphasize that these attractive and repulsive contributions correspond to the van der Waals ones, i.e. $Pr = R T/(v - b)$ and $Pa = p - Pr$. Then, the friction coefficients are separated into a critical isotherm contribution, which in the case of cubic EoS turns out to be a universal curve, and a residual temperature dependent contribution. The κ_a , κ_r , and κ_{rr} parameters are only dependent on the reduced temperature and have been parameterized into universal constants that are related to a specific EoS.

$$\begin{aligned} \hat{\kappa}_a &= \hat{\kappa}_a^c + \Delta \hat{\kappa}_a \\ \hat{\kappa}_r &= \hat{\kappa}_r^c + \Delta \hat{\kappa}_r \\ \hat{\kappa}_{rr} &= \hat{\kappa}_{rr}^c + \Delta \hat{\kappa}_{rr} \end{aligned} \quad (25)$$

$$\begin{aligned} \Delta \hat{\kappa}_a &= \kappa_{a,0,0}(\Gamma - 1) + (\kappa_{a,1,0} + \kappa_{a,1,1}\psi)(\exp(\Gamma - 1) - 1) \\ &\quad + (\kappa_{a,2,0} + \kappa_{a,2,1}\psi + \kappa_{a,2,2}\psi^2)(\exp(2\Gamma - 2) - 1) \end{aligned} \quad (26)$$

$$\begin{aligned}\Delta\hat{\kappa}_r &= \kappa_{r,0,0}(\Gamma - 1) + (\kappa_{r,1,0} + \kappa_{r,1,1}\psi)(\exp(\Gamma - 1) - 1) \\ &\quad + (\kappa_{r,2,0} + \kappa_{r,2,1}\psi + \kappa_{r,2,2}\psi^2)(\exp(2\Gamma - 2) - 1)\end{aligned}\quad (27)$$

$$\Delta\hat{\kappa}_{rr} = \kappa_{rr,2,1}\psi(\exp(2\Gamma) - 1)(\Gamma - 1)^2 \quad (28)$$

where

$$\Gamma = \frac{T_c}{T} \quad (29)$$

and

$$\psi = \frac{RT_c}{P_c} \quad (30)$$

Values for κ_a , κ_r , and κ_{rr} and $\hat{\kappa}_a^c$, $\hat{\kappa}_r^c$ and $\hat{\kappa}_{rr}^c$ can be obtained [22] for the Peng Robinson [30], SRK [29] and PRSV [39] EoS. In this study, when the one parameter model was used, the original Peng-Robinson EoS, with the classical van der Waals mixing rules was used to model the PvT behaviour of hydrogen sulphide and the sour gas fluids. The critical temperature, pressure and acentric factor of hydrogen sulphide were taken from the compilation of Rowley et al. (DIPPR) [40].

When mixtures are considered, the value of the mixture friction coefficients are predicted using the following mixing rules:

$$\eta_{mx} = \eta_{0,mx} + \eta_{f,mx} \quad (31)$$

where the subscript mx indicates the corresponding mixture property. The dilute gas limit mixture is determined with:

$$\eta_{0,mx} = \exp\left[\sum_{i=1}^n x_i \ln(\eta_{0,i})\right] \quad (32)$$

where the subscript i indicates component i . The residual mixture friction contribution is determined with:

$$\eta_{f,mx} = \kappa_{r,mx}P_r + \kappa_{a,mx}P_a + \kappa_{rr,mx}P_r^2 \quad (33)$$

The viscous friction coefficients for the mixture are determined with the mixing rules found in equations (34) to (36).

$$\kappa_{r,mx} = \sum_{i=1}^n z_i \frac{\eta_{c,i} \hat{\kappa}_{r,i}}{P_{c,i}} \quad (34)$$

$$\kappa_{a,mx} = \sum_{i=1}^n z_i \frac{\eta_{c,i} \hat{\kappa}_{a,i}}{P_{c,i}} \quad (35)$$

$$\kappa_{rr,mx} = \sum_{i=1}^n z_i \frac{\eta_{c,i} \hat{\kappa}_{rr,i}}{P_{c,i}^2} \quad (36)$$

Here z_i , a weighted mole fraction, is determined with equations (37) and (38).

$$z_i = \frac{x_i}{MW_i^\varepsilon MM} \quad (37)$$

where

$$MM = \sum_{i=1}^n \frac{x_i}{MW_i^\varepsilon} \quad (38)$$

and

$$\varepsilon = 0.30 \quad (39)$$

For the EOS (used to determine the molar volumes and hence P_r and P_a) in principle, the mixing rules that best describe the fluid phase behaviour should be used.

For the sake of comparison, four other viscosity models were also used to model the viscosity of pure H₂S. These models were SUPERTRAPP, REFPROP, AQUAlibrium and the correlations found in the DIPPR database.

SUPERTRAPP

SUPERTRAPP is a software a package developed by NIST for the prediction of thermodynamic and transport properties of fluid mixtures. The software has been developed for hydrocarbon mixtures, but non-hydrocarbon components found in natural gases are also included [41].

NIST Chemistry Webbook - REFPROP

NIST has also developed a highly accurate software package for fluid thermodynamic and transport properties called *REFPROP*. This package uses the most accurate reference equations for the thermodynamic properties of pure fluid [37,38].

AQUAlibrium

AQUAlibrium is a software package designed for predicting the phase equilibrium in acid gas mixtures, but is also applicable to sour and sweet gas systems. Recent versions of the software include predictions of the transport properties of the fluids using proprietary models [42].

DIPPR

The *DIPPR* database contains a number of equations that can be used to determine the physical properties of pure component systems. The parameters of *DIPPR*'s equations are determined from the screened data found in the component's databank. The database contains a large number of components and equations for the viscosity of vapour phase (1.013 bar) and the saturation liquid phase both as functions of temperature [40].

H₂S VISCOSITY RESULTS

One parameter f-theory:

To include H₂S into the one parameter model used in reservoir fluid systems the polarity and hydrogen bonding terms in the dilute gas term were required to be estimated. Without these terms, the non-polar form of Chung et al.'s [35] model was incapable of accurately representing the low density data. As such, the hydrogen bonding term was optimally fit to the dilute gas data calculated by the reference equation of state. As can be seen in Figure 3 the addition of these terms reproduces the experimental data very well. The hydrogen bonding correction factor, κ , in equation (19) was determined to be 0.0539 with an AAPD of 2.1% and a bias of 0.06% over a 410 K (186.6 – 596.6 K) temperature range.

Once the dilute limit was determined, the rests of the viscosity-temperature-pressure space was used to determine the critical scaling viscosity coefficient for hydrogen sulphide. Data was generated from the reference viscosity equation at reduced pressure intervals of 0.03 – 1.11 and reduced temperature intervals of 0.54 (200 K) – 1.6 (597 K). A characteristic viscosity scaling parameter, η_c , of 317.985 μ P with an AAPD of 1.8% and a bias of 0.05 % was determined from the reference data.

Overall, the one parameter model represents the saturation data reasonably well and the 1.013 bar gas viscosity very well. The results from the one parameter f-theory are compared to the experimental saturation data and the results from the reference viscosity equation in Figures 4 and 5. The deficiencies of the modelling approach at the low temperature region are expected as the friction theory was originally developed for lighter fluids well away from the triple point. As can be seen in Figure 6, the one parameter model, does not do a good job of representing the super-critical data of Monteil et al. [9], but as stated before these data are considered to be poor and are not of significance.

Figure 3 also shows the 1.013 bar gas viscosity determined from *DIPPR*, *AQUALibrium*, *SUPERTRAPP* and *REFPROP* are all quite similar and compare well with that obtained from the one parameter f-theory and viscosity reference equation. As expected the results from the viscosity reference equation, the generalized f-theory, reproduce the experimental data the best.

The results from all the models vary significantly when the saturation liquid viscosity is considered. Figures 4 and 5, compare the experimental results with those obtained from the six viscosity modelling techniques. Results from molecular dynamic simulation [14] are included in these plots and illustrate that the data from Steele et al. are exceptionally high. *AQUALibrium* underestimates the liquid viscosity at all temperatures. *DIPPR*, *SUPERTRAPP* and *REFPROP* tend to overestimate the viscosity at all temperatures, except at the temperatures close to the triple point. The *DIPPR* correlation matches the higher temperature data better than these two models.

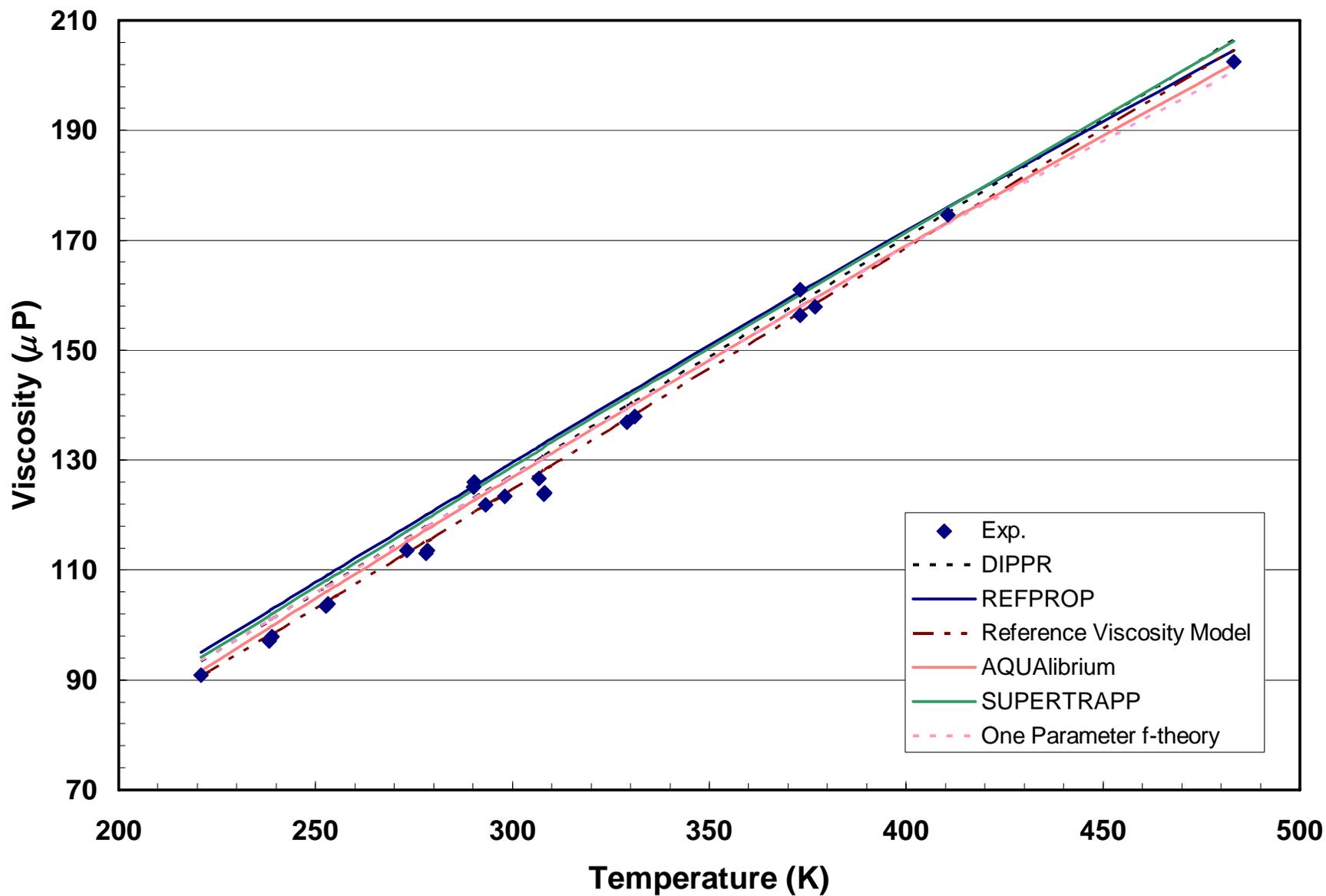


Figure 3. Comparison of Calculated and Experimental H₂S Vapour Viscosity at 1.013 bar.

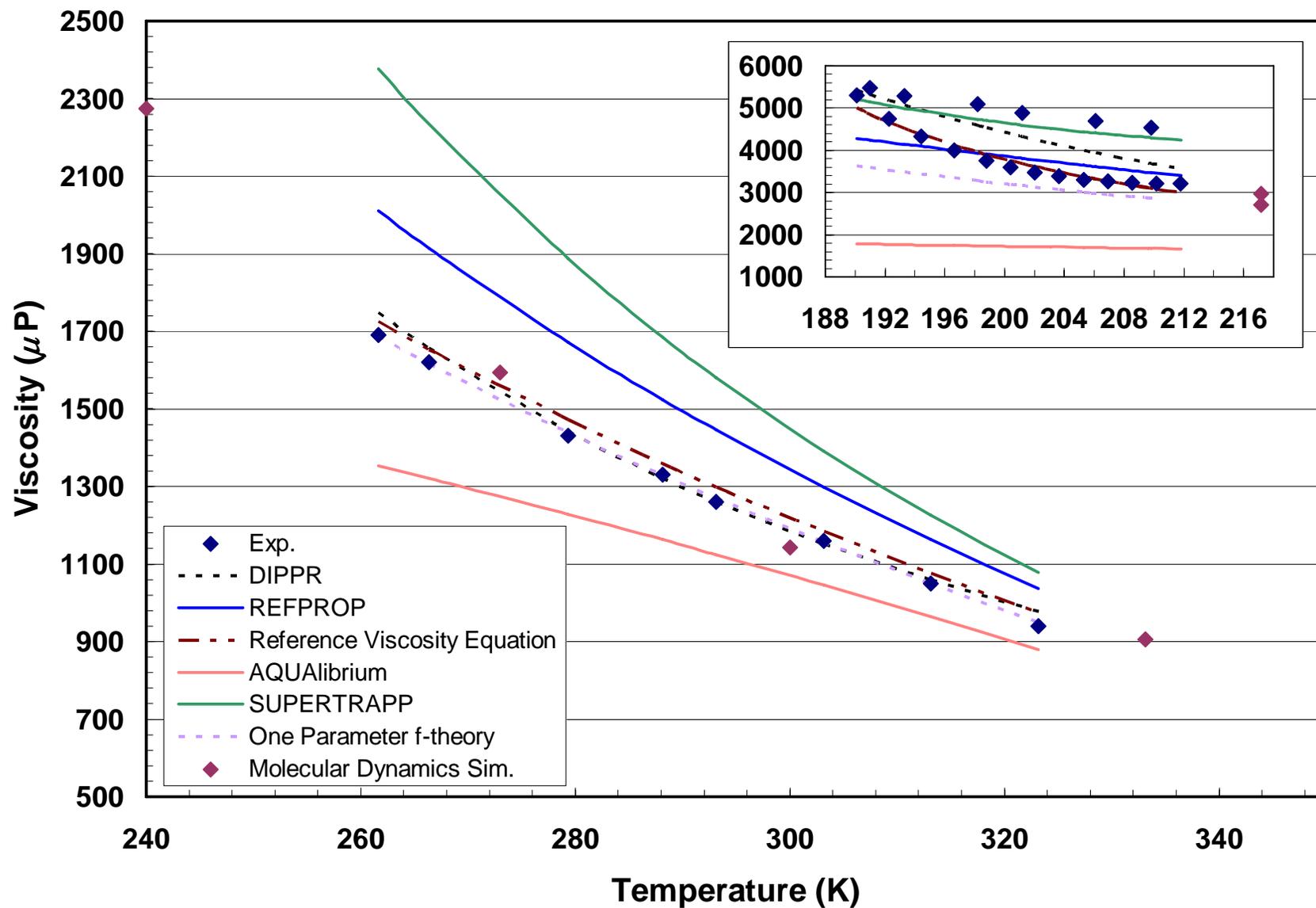


Figure 4. Comparison of Calculated and Experimental H₂S Liquid Viscosity at Saturation Conditions.

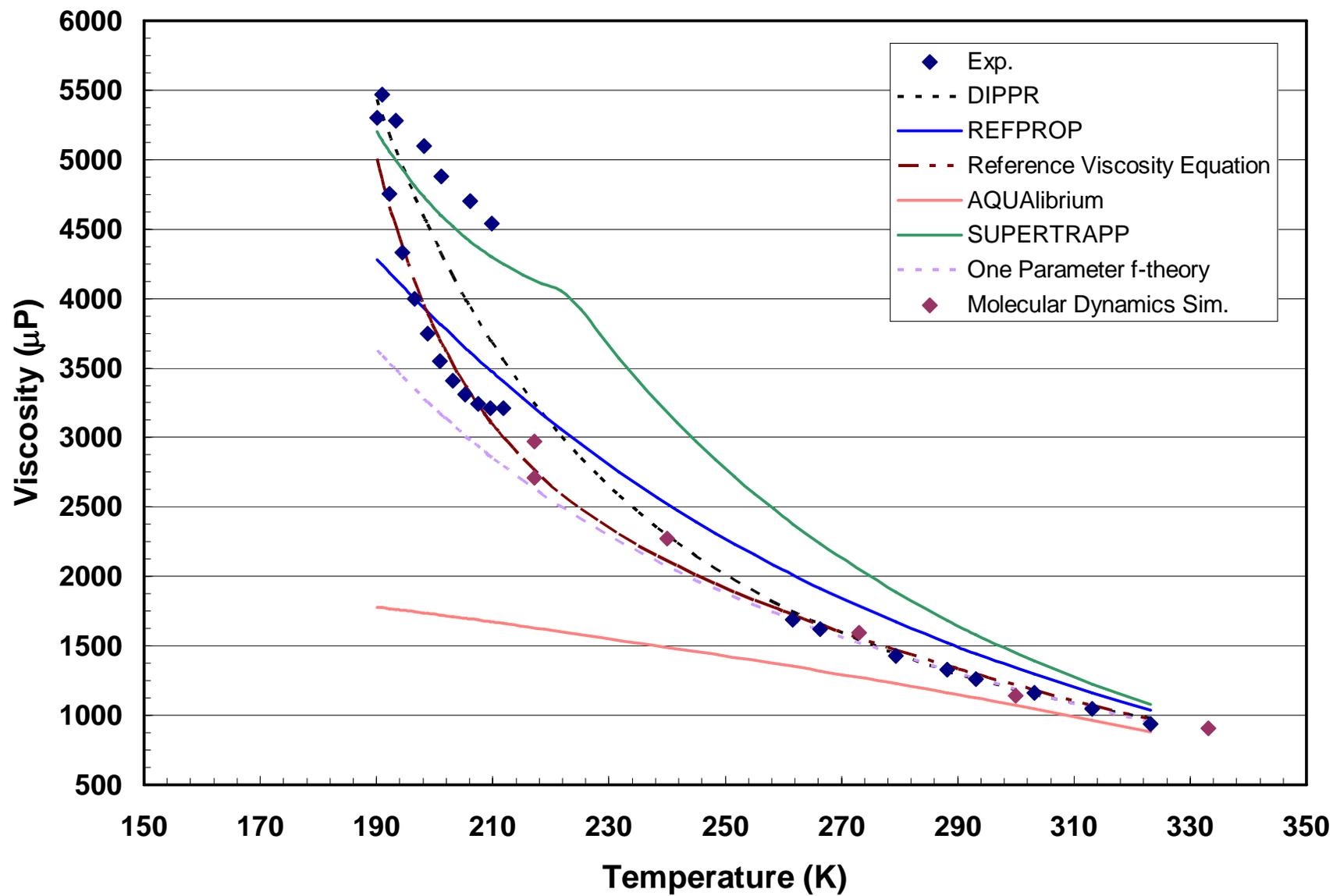


Figure 5. Overall Comparison of Calculated and Experimental H₂S Liquid Viscosity at Saturation Conditions.

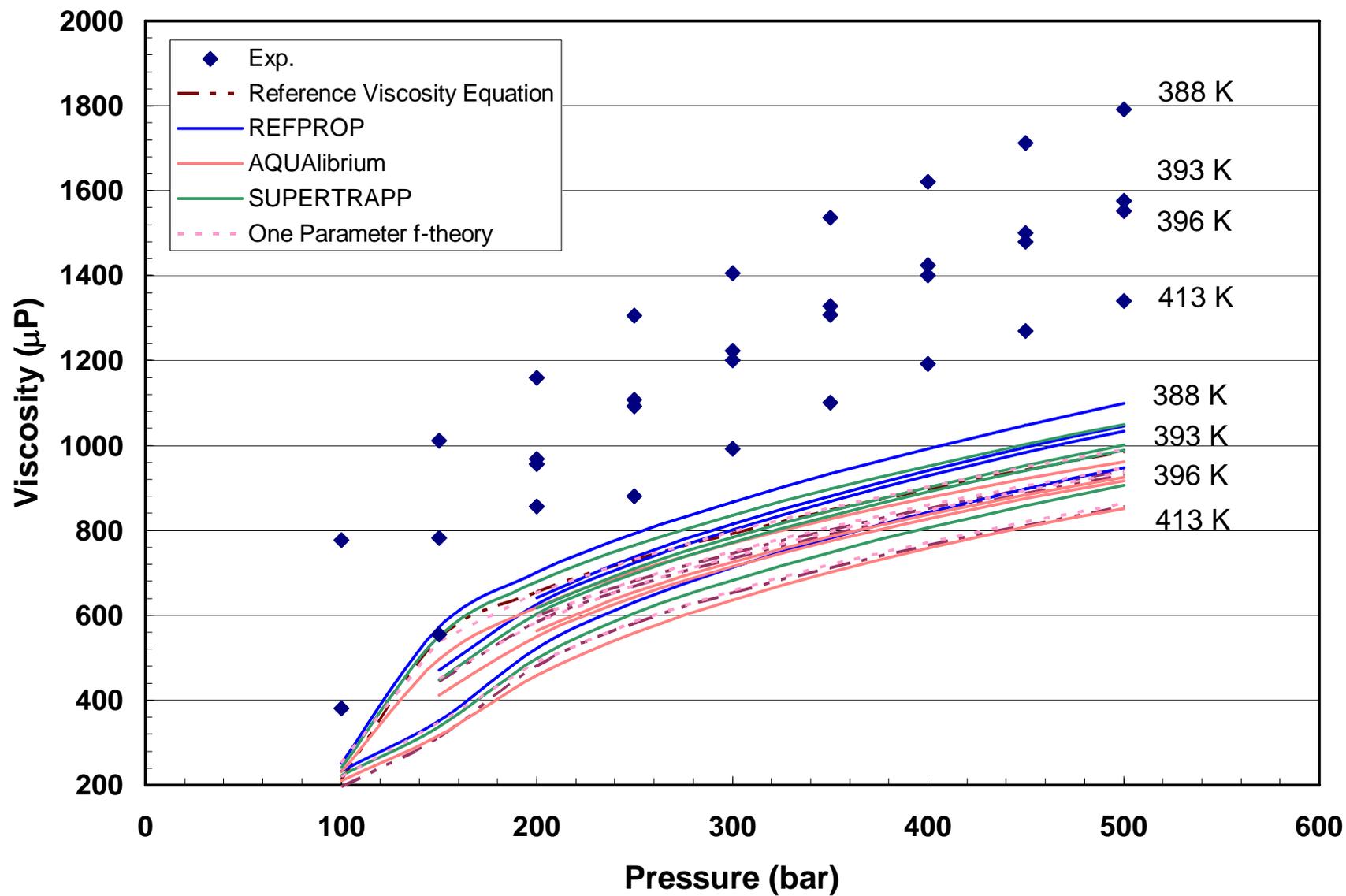


Figure 6. Comparison of Calculated and Experimental H_2S Liquid Viscosity at Supercritical Conditions.

The viscosity reference equation of state reproduces the experimental data very closely over essentially the full temperature range. The one parameter f-theory does a very good job of reproducing the temperature region above 200 K. Its ability to reproduce the low temperature results diminishes with decreasing temperature. The one parameter f-theory was developed at temperatures well away from the triple point which results in its poor ability to capture the physics at temperatures near the triple point. In this region, as the temperature approaches the triple point the viscosity increases dramatically and this was not captured in the original development. In fact, this phenomena also occurs in CO₂ and the one parameter f-theory has difficulty in the near triple point region as well.

Despite, extending the model beyond its capabilities to the near triple point region, the model can reproduce the data to within 10% at a temperature of 200 K. No model, except for the DIPPR liquid viscosity correlation, other than the viscosity reference equation captures the triple point region well. Temperatures of this scale are rarely if never experienced in the sour gas processing or acid gas injection industries and therefore the one-parameter f-theory model is fully applicable within the full range of fluids expected operating conditions.

As described earlier the supercritical data of Monteil et al. [9] were rejected in the development of the reference equation. As can be seen in Figure 6, no model not even the viscosity reference equation can reproduce these data. The data are exceptionally high when compared to the results viscosity reference equation at the same conditions. In addition the data appear to have a much higher change with pressure.

SOUR GAS VISCOSITY RESULTS

One parameter f-theory:

Unfortunately, there are few H₂S mixture viscosity experimental data points relevant to the gas processing industry available in the open literature. In fact the amount of mixture data is significantly less than that for pure H₂S. A comprehensive literature review revealed only one source of data [43,44]. The databank of data used in these references contains a large number of data for reservoir fluids, however only eight viscosity data points of samples containing H₂S are available. The H₂S content of these fluids ranges from 0.02 to 70.03 mole %. The temperatures and pressures appear to be at reservoir conditions; however no further information including experimental method or accuracy is given. The identification numbers of the fluids tested were: Koc46, Koc59, 1111, 1881, 2076, 84, 439 and 926.

As mentioned previously, the original version of the Peng-Robinson EOS was used in combination with the one parameter f-theory. The critical temperatures, pressures and acentric factors of nitrogen, carbon dioxide hydrogen sulphide and the C₆ hydrocarbon components (methane – n-hexane) were taken from the compilation of Rowley et al. (DIPPR) [40]. When a C₇₊ fraction was present the critical temperature, critical pressure and acentric factor was determined with the supplied C₇₊ fraction molecular weight. The necessary equation of state parameters for the C₇₊ fraction was estimated using equations (40) - (42), which are empirical correlations based the properties of normal alkanes [24].

$$T_c = -423.587 + 210.152 \ln(MW) \quad (40)$$

$$P_c = f_c \exp(9.67283 - 4.05288MW^{0.1}) \quad (41)$$

$$\omega = \exp\left(8.50471 - \frac{15.1665}{MW^{0.1}}\right) \quad (42)$$

In these three equations, MW is in g/mol in order to obtain T_c in K and P_c in bar. The parameter f_c in equation (41) represents a perturbation factor away from the $f_c = 1$ corresponding to n-alkanes. Typically, the perturbation parameter is iteratively modified (tuned) until the saturation pressure of the fluid of interest is matched [27]. Since, no saturation data was available, the f_c parameter could not be tuned and a $f_c = 1$ was used. Since the C_{7+} composition was not significantly high, no attempts were made to split the C_{7+} fraction into smaller pseudo-components.

Without more than one viscosity data point to tune the C_{7+} fraction critical scaling parameter, η_c , to, the $\eta_{c,C_{7+}}$ was assumed to be the value of that of the corresponding n-alkane determined with the modified Uyehara and Watson [50] correlation [24]

$$\eta_c = 7.9483 \frac{\sqrt{MW} P_c^{2/3}}{T_c^{1/6}} \quad (43)$$

Naturally the amount of C_{7+} fraction and the way it is characterized will affect the results and the calculated viscosity could be significantly improved if the relaxed form of the Uyehara and Watson [50] correlation [24] was used:

$$\eta_c = K_c \frac{\sqrt{MW} P_c^{2/3}}{T_c^{1/6}} \quad (44)$$

and the K_c parameter was adjusted until the available viscosity data was matched. Since there was only one data point available for each fluid the viscosity characterization technique of [24] and [27] was not used. As such, the obtained results are predictions based on the pure fluid component properties and the C_{7+} fraction properties determined with the techniques described above.

A variety of binary interaction parameters for the Peng-Robinson EoS were considered. H_2S binary interaction parameters were obtained from Carroll and Mather [45] or Stamataki and Magoules [46] all other binary interaction parameters were taken from either Nagy and Shirkovskiy [47] or Knapp and Doring [48,49]. The combination of the binary interaction parameters from Knapp and Doring [48,49] and Stamataki and Magoules [46] gave the best results in the viscosity and in the Z – factor (al be it slightly). Overall the one parameter f-theory predicted the viscosity of these eight fluids to within 13.1 %.

This work's predictions are better than the models tested by Elsharkawy [43]. Some of the models tested by Elsharkawy included viscosity models only applicable to the gas phase. One significant advantage of the f-theory is that it can be used to the model the viscosity of fluids ranging from dilute gaseous to dense heavy oils. This one equation applicable to the vapour and liquid phases, similar to an equation of state, ensures that there is no discontinuity in the T - η - P space. As discussed by Elsharkawy [43], the accuracy of the tested models depends on the amount of the C_{7+} fraction; this

is not true with the f-theory. Based on the pure and sour gas mixture results, the inclusion of H₂S extends the one parameter f-theory model to sour systems.

The results are quite satisfactory despite the limited number of data points and the unascertained quality of the data. The viscosity of the high H₂S fluid was quite good, suggesting that this approach may be extended to acid gas injection schemes. Although more testing of the model is warranted when more data relevant to these schemes becomes available.

CONCLUSIONS AND RECOMMENDATIONS

The optimal design of an acid gas injection scheme requires various physical properties. The viscosity is important in order to establish the optimum pipeline diameter for the transport of the acid gas from the compressor to the injection well and for the estimation of the pressure loss due to fluid friction in the well bore. This is especially true for the larger injection schemes. In addition, the viscosity is an important parameter for performing reservoir calculations.

As such, an exhaustive literature survey to obtain all the pure hydrogen sulphide viscosity data available was performed. All the published data was reviewed and the f-theory was successfully applied to obtain a H₂S reference viscosity model. Although, based on limited data, this model has a strong theoretical background and with the critical evaluation of the data and sound physical reasoning this model gives superior modelling results over the T - η - P surface for H₂S. The accurate results from the reference equation was then used to obtain the necessary scaling parameters used in the one-parameter f-theory models which has been shown to model the viscosity of a wide variety of reservoir fluids under broad conditions. When tested against the only available sour gas data, the predictions from the one parameter model were quite satisfactory when compared to previous modelling investigations.

The literature review and the development of the H₂S reference viscosity model identified significant regions where additional data are needed to fill voids, resolve discrepancies of existing data sets and to extend regions where the viscosity may be insufficiently modelled with the current techniques. New experimental measurements or Molecular dynamics simulations, based on the findings are required to expand the data set, not only for pure H₂S but for mixtures necessary found in the sour gas treating and acid gas injection industries.

Increasing the available data for viscosity of hydrogen sulphide is only the starting point. The acid gas found in injection schemes is a mixture of H₂S, CO₂, light hydrocarbons, and water. It is the mixture properties that are important in the design of an optimum acid gas injection scheme. It should also be pointed out that the conditions (temperature and pressure) of the experiments should be at the relevant operating conditions found in industry.

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