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Dynamic viscosity estimation of hydrogen sulfide using a predictive scheme based on molecular dynamics.

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Abstract

An approach based on molecular dynamics results on Lennard-Jones spheres is proposed to model the viscosity of hydrogen sulfide, H₂S. The molecular parameters, that have a strong physical meaning, are the depth of the potential, and the length at which the potential is null (the “molecular diameter”), which take into account the dipolar moment of the hydrogen sulphide through an isotropic dipolar approximation. The interest of the method is that the adjustment does not involve any viscosity data because only density values have been used in order to estimate the molecular parameters. Consequently, the model is entirely predictive. A comparison between the data generated by our model, REFPROP7 and REFPROP8 database and the few available experimental viscosity data (dilute gas and saturated liquid) is performed and clearly demonstrates the performance of this predictive model. It is even shown that this model is, without fitting, slightly better than REFPROP7 and REFPROP8 which uses viscosity experimental database to adjust their parameters. In addition, in typical petroleum reservoirs conditions, it is shown that non negligible deviations appear when comparing results predicted by REFPROP7, REFPROP8 and the model proposed. Due to its predictive nature, we believe that the values evaluated by the proposed model make sense in such reservoir conditions, at least for industrial purposes. Moreover, the scheme proposed is

shown to be very easily extended to deal with mixtures involving H₂S with the limit that the Lennard-Jones fluid model is appropriate for the other species of the mixtures.

Keywords:

Hydrogen sulfide; Viscosity; Molecular Dynamics; Lennard-Jones; Acid gas.

1. Introduction

Acid gas mixtures (ie natural gases containing hydrogen sulfide H_2S and/or carbon dioxide CO_2) are often encountered in the petroleum industry. For the systems containing hydrogen sulfide, experiments on their thermophysical properties are very scarce because of the very high toxicity of H_2S which leads to very complicated safety procedures for the experimentalists. This is especially true for the high pressures and temperatures conditions of petroleum reservoir. As we recently emphasized [1], this lack of knowledge is particularly apparent concerning transport properties. Concerning the dynamic viscosity, the available experimental database is very small. The reader could find a presentation of the works available in the literature in a recent work [2]. It is worth to mention the work of Liley et al. [3], which proposes after critical analysis of the available data, a table with 18 values between 190 and 350 K for the saturated liquid (pressure up to 6 MPa) and 21 values for the dilute gas as a function of temperature between 250 and 500 K. For the dilute gas these authors propose an equation after the analysis of several experimental data sets. The analysis recently presented in [2] confirms also the fact that the number of confident experimental viscosity data is very small. In particular, it seems that the data set of Monteil et al. [4] at high pressures and temperatures should be not considered [2] as these data exhibited inconsistencies with the rest of the data set.

As experiments are difficult to perform on H_2S , alternatives are highly encouraged. In [2] the authors propose a hydrogen sulfide viscosity modeling based on the friction-model [5]. The authors propose a correlation in order to evaluate the viscosity in larges pressure and temperature range. They give a hydrogen sulfide reference friction theory model, which involve 18 adjustable parameters (and 4 more parameters for the dilute gas). But as the number of experimental data is too low for their fitting procedure, they have to make some assumptions on the H_2S viscosity behavior. They acknowledge that their model is sensitive

and requires a good database to be regressed against for optimal performance. 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 may show a similar qualitative behaviour as H₂S, based on supposed similarities between hydrogen sulfide and carbon dioxide or ethane. They indicate that their H₂S model has been developed by combining the few available reliable H₂S data with low pressure scaled CO₂ data and elevated pressure scaled C₂H₆ data. Then, they adjusted the 18+4 parameters (parameters without physical meaning). Next to that, the general reference friction-theory model is used as a reference for the tuning of so called one-parameter viscosity model. It should not be forgotten that in fact this modeling is made with a database not only based on experimental data, but also on scaled CO₂ and C₂H₆ viscosities (without any explanation about the scaling nor the number of data evaluated in such way). Nevertheless, due to the lack of information on the dynamic viscosity of H₂S, this model has been implemented in the software REFPROP 8 [6] developed by the National Institute of Standards and Technology (NIST), because a better model is lacking.

In order to avoid to make speculative assumptions on the values of the viscosity of the H₂S, we propose in this paper another approach, based on molecular dynamics results for Lennard-Jones spheres, in which only 2 adjusted molecular parameters with physical meaning are used, only adjusted to density data [1]. These parameters are ϵ , the strength of the potential, and σ the length at which the potential is zero (the “molecular diameter”), which take into account the dipolar moment of the hydrogen sulphide through an isotropic dipolar approximation [7]. The adjustment does not involve any viscosity data and consequently the model is entirely predictive. As no adjustment has been done to viscosity data, the comparison between the data generated by our model and the few available viscosity data is significant for the performance and of the physical meaning of the model, and we can therefore expect that the values evaluated at pressures and temperatures outside the pressure and temperature range of the

available data could be considered significant, at least for industrial purposes, particularly in dense states at high pressure and high temperature, as in reservoir conditions. Finally, it is mentioned here that, in a previous study [1], we already have given some molecular dynamic results for the viscosity of H₂S, but we did not develop in this previous work a model which is easy to implement in computing software.

2. Modeling

2.1. Interaction potential

In this work, it is assumed that the H₂S molecule can be correctly described by a one center spherical particle (united atom). In addition, to describe intermolecular interactions occurring between two particles, it is assumed that the total interaction potential can be simply described by the sum of a non polar contribution and a contribution due to the dipolar moment of the hydrogen sulfide:

$$U_{Tot} = U_{non-polar} + U_{polar} \quad (1)$$

To describe the non polar interactions, the usual Lennard-Jones 12-6 (LJ) effective potential is used:

$$U_{non-polar} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

where ϵ is the potential strength, σ the length at which the potential is zero (the “molecular diameter”) and r the intermolecular separation.

The dipolar contribution, it is modelled by a Keesom potential [8], which writes for pure H₂S:

$$U_{polar} = -\frac{1}{k_B T} \frac{\mu^4}{3r^6} \quad (3)$$

where μ is the dipole moment, k_B the Boltzmann constant and T the temperature.

It should be mentioned that such description of the dipolar interaction, corresponds to a combination of a centrally located dipole expansion combined with an averaging over molecular orientations (i.e. isotropic potential). This isotropic assumption implies that such an approach remains valid only as long as structural effects are not large, i.e. when the energy involved by the polar interaction is low as compared to the thermal energy $k_B T$. Such assumption for H₂S is acceptable [1,9] as long as temperature is not too low (typically higher than 200 K), especially in dense systems.

For our purpose, a very interesting feature of such formulation of the polar contribution is that the total potential, eq. (1), can be rewritten as a simple LJ potential with temperature dependent molecular parameters, σ_{pol} and ϵ_{pol} :

$$U_{Tot} = 4\epsilon_{pol} \left[\left(\frac{\sigma_{pol}}{r} \right)^{12} - \left(\frac{\sigma_{pol}}{r} \right)^6 \right] \quad (4)$$

where σ_{pol} and ϵ_{pol} are given by:

$$\sigma_{pol}^6 = \frac{\sigma^6}{F} \quad (5)$$

$$\epsilon_{pol} = \epsilon F^2 \quad (6)$$

where

$$F = 1 + \frac{\mu^4}{12k_B T \epsilon \sigma^6} \quad (7)$$

The potential described by eq. (4) will be noted isotropic dipolar potential (IDP) in the following. It is important to note that such formulation of the total interaction potential allows treating the H₂S dipolar molecule as a simple LJ sphere with temperature dependent molecular parameters and, thus, permits the use of the numerous literature results on the LJ fluid as will be shown later.

2.2. H₂S molecular parameters

The adjustment of two molecular parameters, ϵ and σ , of the H₂S molecule has been done in a previous work [1]. The following procedure was applied [1]: using for the dipole moment of the H₂S, the commonly accepted literature value $\mu=0.9\text{D}$ [10], three different state points have been considered, one on the liquid saturation curve ($T=273\text{ K}$, $P=1.028\text{ MPa}$), and two at high temperature/high pressures ($T=498.2\text{ K}$ and $P=10.02$ or 39.993 MPa) for which experimental density results exist [11,12]. Then, for these three state points, using constant pressure molecular dynamics simulations (NPT), σ and ϵ have been obtained by fitting the experimental densities. The molecular parameters obtained are summarized in Table 1. In Table 1 the values of the dipole moment (taken from [10]) and of the molecular mass are also given.

3. Results

3.1. H₂S density

Among the various equations of state (EoS) that represent correctly the thermodynamic behavior of the Lennard-Jones fluid, we have used the theoretically founded EoS of Kolafa and Nezbeda [13], which is based on a perturbed virial expansion. In a previous work [1], it has been shown that this EoS combined with the potential given by eq. (4) and the parameters provided in Table I allows a reasonable estimation of the H₂S density when T and P are fixed. More precisely, this scheme yields an Average Absolute Deviation (AAD) for ρ equal to 0.51 % with a Maximum Deviation (MxD) of 0.97 % [1] when compared to the subcritical data of Ihmels and Gmehling [12] containing 206 points ($T=273\text{-}363\text{ K}$, $P=3\text{-}40\text{ MPa}$). Recall here that only 3 density data points have been used in order to adjust the 2 parameters ϵ and σ

3.2. H₂S dynamic viscosity

In previous work [14], using extensive molecular dynamics simulations, we have developed an empirical correlation which allows an accurate estimation of the viscosity of the Lennard-Jones fluid for a wide range of thermodynamic states (gas, liquid and supercritical) for a given set of density and temperature. More precisely, in the range $0 \leq \rho/\rho_c \leq 4.05$ and $0.45 \leq T/T_c \leq 4.53$ (where ρ_c and T_c are respectively the critical density and the critical temperature) the deviations between the correlation and the molecular simulations were always lower than 6 % [14]. When applied to the IDP model this correlation can be written as:

$$\eta = \frac{(m\epsilon_{pol})^{1/2}}{\sigma_{pol}^2} \left[\frac{5}{16\Omega_v} \sqrt{\frac{T^*}{\pi}} + a_1(e^{a_2\rho^*} - 1) + a_3(e^{a_4\rho^*} - 1) + \frac{a_5}{(T^*)^2}(e^{b_6\rho^*} - 1) \right] \quad (8)$$

where T^* is the dimensionless temperature ($=k_B T/\epsilon_{pol}$), ρ^* the dimensionless density ($=\rho\sigma_{pol}^3/m$), a_i are the numerical coefficients for the LJ fluid [14] that are given in Table 2, Ω_v is the collision integral that can be estimated using the correlation of Neufeld et al. [15] and m is the molecular weight. As can be seen from eq. (8), this correlation includes of a low density term described by a Chapman-Enskog approximation [16] and a residual viscosity contribution.

It should be noted that, to apply eq. (8) when the input thermodynamic conditions are not T and ρ , but the more usual set T and P , one should first use the LJ EoS of Kolafa and Nezbeda [13] to calculate ρ from the given T and P . This procedure has been applied in the following.

Results provided by the viscosity correlation for H₂S with the molecular parameters given in Table 1, using eq. (8) and the Kolafa and Nezbeda EoS, are shown in Figures 1 (dilute gas) and 2 (saturated liquid). It is important to recall again that these results are completely predictive as long as the 2 molecular parameters, ϵ and σ , have been adjusted to a thermodynamic property (density) and not on a transport property (dynamic viscosity). These

results have been compared, see Figures 1 to 4, with the database proposed by Liley et al. [3] which claims an uncertainty of 4 % for the dilute gas values and 20 % for the saturated liquid values. In addition, results provided by the software REFPROP 7 [17] and REFPROP 8 are plotted in figures 1 to 4 at the same conditions. It should be noted that, after inquiry to the REFPROP software editor, [18], it seems that REFPROP7 is based on an empirical correlation of the same kind as the one used in ref. [19] which is adjusted to an experimental database.

Concerning the results for dilute gases, see Figures 1 and 2 and Table 3, it appears that our correlation yields excellent results compared to the values given in the database of Liley et al. [3] database within their estimated uncertainties (4 %). This result is not so surprising since at low density the Chapman-Enskog viscosity contribution in eq. (8) dominates. Furthermore, at these thermodynamic conditions (i.e. low density and not too low temperature), the isotropic dipolar approximation, eq. (3), is completely acceptable.

It should be mentioned, that despite slight differences at low temperatures, both REFPROP 7 and REFPROP8 provide good estimations as well for these low density conditions, see Figures 1 and 2 and Table 3.

The viscosity results provided by this entirely predictive scheme for saturated liquid are more than acceptable when compared to the values of the database of Liley et al., see Figures 3 to 4 and Table 3. Moreover, what is interesting is that this entirely predictive scheme performs better than REFPROP7 and slightly better than REFPROP8, see Table 3. Recall here that, for these two models, an experimental viscosity database has been included in the adjustment of the parameters. Besides, it is worth to mention, see Figure 4, that all three schemes tend to underestimate the viscosity compared to the values of the database of Liley et al. when approaching the critical point.

In addition, the trends obtained by our new approach are really consistent, i.e. at low temperature (below 270 K) the underestimation increases when temperature decreases, see Figure 4, which is certainly due to the IDP limitations for such conditions. Besides, for the saturated liquid, if the density deduced from REFPROP8 (which uses reference [20]) are used instead of those deduced using the Kolafa-Nezbeda EOS, the viscosity correlation, eq. (8), yields slightly better results with AAD=4.3 % and MxD=13.9 % instead of 5.5% and 15.6 %, see Table 3.

The thermodynamic conditions of interest for the petroleum industry are in general between 273.15 and 423.15 K and between 10 and 140 MPa. Unfortunately, for such conditions only the experimental data sets of Monteil et al. [4] are available, and it has been shown that these values should be not considered [2] as these data exhibited inconsistencies. So, for pressures from 10 to 140 MPa, with a step a 10 MPa, and temperatures from 273.15 to 423.15 K, with a step of 50 K, REFPROP7, REFPROP8 and the new scheme have been used to estimate viscosities, see Figure 5. As a preliminary test of the validity of the results provided by the proposed scheme for such thermodynamic conditions, nonEquilibrium MD simulations have been performed at $T=273.15$ K, $P=10$ MPa and $T=423.15$ K, $P=140$ MPa using the procedure described in a previous work [1]. For these two dense states, we obtain by MD simulations respectively $\eta = 168 \pm 8 \cdot 10^{-6}$ Pa.s and $143 \pm 6 \cdot 10^{-6}$ Pa.s whereas the proposed scheme based on eq. (8) yields $166 \cdot 10^{-6}$ Pa.s and $144 \cdot 10^{-6}$ Pa.s. Such good agreement is not surprising as long as eq. (8) is able to represent MD results of LJ sphere [14] (with a MxD below 6 %) for a wide range of thermodynamic conditions that encompass those studied in this work.

From the results provided in Figure 5, it appears that in all cases the values predicted by the new scheme are between those predicted by REFPROP7 and REFPROP8, and generally closer to those of REFPROP8. In addition, the larger the viscosity, the larger the deviations between results from the different models (between REFPROP7 and REFPROP8 the

deviation reaches 34.6% at P=140 MPa and T=273.15 K). Compared to our scheme, REFPROP7 yields an AAD=12.2 % with a MxD=18.5 % and REFPROP8 an AAD=4.4% with a MxD=15.4 %.

It is important to note that, because the new scheme is completely predictive, and the IDP is physically acceptable for not too low temperature, the results provided by this correlation for the high pressures conditions tested here should be as good as those given at these conditions in the database of Liley et al.. That is not necessary the case for the fitted approaches such as those used in REFPROP7 and REFPROP8 as they have been adjusted to a rather limited experimental database. Hence, the reliability of the predictions of such models outside the range of the conditions of the experimental database is probably more questionable as shown by the differences noted in Figure 5.

3.3. Extension to mixtures

One nice feature of the scheme proposed is that it can be very easily extended to deal with mixtures involving H₂S under the condition that the LJ fluid model is appropriate for the other species of the mixtures. To do so, once the molecular parameters (m_i , σ_{ii} , ϵ_{ii}) of each compound i are known (plus the dipolar moment of H₂S), one has to use the van der Waals one fluid approximation [21] which consists in lumping the different compounds of the mixture into one equivalent pseudocomponent using the molar fraction x_i :

$$m_x = \sum_i x_i m_i \quad (10)$$

$$\sigma_x^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (11)$$

$$\epsilon_x \sigma_x^3 = \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3 \quad (12)$$

The cross molecular parameters, ϵ_{ij} and σ_{ij} are defined by a set of combination rules which are usually the Lorentz-Berthelot (LB) ones:

$$\sigma_{ij} = \left(\frac{\sigma_{ii} + \sigma_{jj}}{2} \right) \quad (13)$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \quad (14)$$

The “equivalent” pure pseudo-compound so defined, having the molecular parameters m_x , ε_x and σ_x , is supposed to mimic the behaviour of the studied mixture.

Three H₂S rich mixtures in typical petroleum reservoir conditions, for which experimental results exist [22] have been used as a test of this scheme for mixtures, see Table 4 for compositions. To obtain the molecular parameters of the other species involved in those mixtures, except for CH₄ for which the widely used parameters from Möller et al. [23] have been used, the relations proposed by Chung et al. [10] have been used for each compound:

$$\sigma = 0.809V_c^{1/3} \quad (15)$$

$$\varepsilon = \frac{k_B T_c}{1.2593} \quad (16)$$

where the critical molar volume, V_c , and critical temperature, T_c , have been taken from the reference [10].

Results provided in Table 4, clearly show that the proposed correlation is able to yield a very reasonable estimation of the viscosity of such H₂S rich mixtures (acid gases). In addition, using the LB rules, constant pressure nonequilibrium MD simulations (following the procedure described in a previous work [1]) have been performed on these three acid gas mixtures (with a lumping of some compounds when mole fraction is below 0.1 %). It shown in Table 4 that these MD results are consistent with those coming from the correlation which shows that the van der Waals one-fluid approximation is efficient for such mixtures (care should be taken when asymmetric mixtures are involved [24, 25]). Thus, deviations between correlation and experimental results may be probably ascribed to the limitations of the LJ model to represent non spherical molecules.

4. Conclusion

The approach proposed in this paper to estimate hydrogen sulfide viscosity is based on molecular dynamics results, with only 2 adjusted molecular parameters with physical meaning, adjusted to experimental density data. These parameters are ϵ , the strength of the Lennard-Jones potential, and σ the length at which the potential is zero, the “molecular diameter”, which take into account the dipolar moment of the hydrogen sulphide through an isotropic dipolar approximation (such an approximation should be taken with care at temperature below 200K in dense fluids). The interest of the method is that the adjustment does not involve any viscosity data (only three equilibrium experimental densities have been used) and so the model is entirely predictive.

Using this approach, it appears clearly, at the conditions for which H₂S experimental results exist, dilute gas and saturated liquid, that the proposed predictive scheme is able to provide a very good estimation of the viscosity of H₂S. In addition, it is shown that the results provided by this predictive scheme are even better than those obtained using the REFPROP7 and REFPROP8 software that use fitted parameters which are based on database of experimental viscosity values. Nevertheless, all three models show non negligible deviations (> 10 %) when approaching the critical point and at the lowest temperatures (< 200 K).

At petroleum reservoir conditions (P=10-140 MPa, T=273.15-423.15 K), a comparison between the results provided by our model, REFPROP7 and REFPROP8 have shown that non negligible discrepancies may appear. As no adjustment of the proposed model has been done on viscosity data, and as the LJ + IDP makes sense for not too low temperature, we can consequently believe that the values evaluated by the proposed method for these thermodynamic conditions outside the range of conditions of the available experimental data could be considered significant, at least for industrial purposes.

Finally, the scheme proposed is shown to be very easily extended to deal with mixtures involving H₂S (acid gas) with a reasonable success, as shown on three mixtures, with the limit that the LJ fluid model is appropriate for the other species of the mixtures.

List of symbols

k_B	Boltzmann's constant
m	molecular weight (kg.mol ⁻¹)
P	pressure (MPa)
r	intermolecular separation (Å)
T	temperature (K)
T_c	critical temperature (K)
T^*	dimensionless temperature
U	interaction potential (J.mol ⁻¹)
V_c	critical molar volume (m ³ .mol ⁻¹)
x	mole fraction

Greek letters

ε	potential strength (J.mol ⁻¹)
η	viscosity (μPa.s)
μ	dipole moment (D)
ρ	density (kg.m ⁻³)
ρ_c	critical density (kg.m ⁻³)
ρ^*	dimensionless density
σ	Molecular diameter (Å)
Ω_v	collision integral

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Figure legends:

Figure 1: H₂S viscosity in the dilute gas region: data of Liley et al. [3] (◆), eq. (8) (○), REFPROP7 (Δ) and REFPROP8 (□)

Figure 2: Deviations, compared to data of Liley et al. [3], for H₂S viscosity at dilute gas conditions for: eq. (8) (○), REFPROP7 (Δ) and REFPROP8 (□)

Figure 3: H₂S viscosity of the saturated liquid: data of Liley et al. [3] (◆), eq. (8) (○), REFPROP7 (Δ) and REFPROP8 (□)

Figure 4: Deviations, compared to data of Liley et al. [3], for the H₂S viscosity of the saturated liquid yielded by: eq. (8) (○), REFPROP7 (Δ) and REFPROP8 (□)

Figure 5: H₂S viscosities at high pressure estimated by the various approaches tested in this work, the new scheme (○), REFPROP7 (Δ) and REFPROP8 (□), for T=273.15 K, upper left figure, T=323.15 K, upper right figure, T=373.15 K, lower left figure and T=423.15 K, lower right figure.

Tables:Table 1: H₂S molecular parameters used in this work (from ref [1]).

	σ (Å)	ε (J.mol ⁻¹)	μ (D)	m (kg.mol ⁻¹)
H ₂ S	3.688	2320	0.9	0.034082

Table 2: Coefficients used in the viscosity correlation, equation (8) (from ref [14])

i	1	2	3	4	5	6
a_i	0.062692	4.095577	-8.743269.10 ⁻⁶	11.124920	2.542477.10 ⁻⁶	14.863984

Table 3: Deviations (in percentage), compared to the data of Liley et al. [3], for the H₂S viscosities values provided by the new correlation, REFPROP7 and REFPROP8 in low density gases ($P=0.1013$ MPa and $T=250-500$ K) and for the saturated liquid ($T=190-350$ K).

	New scheme	REFPROP7	REFPROP8
AAD Gas	1.8	1.9	1.9
MxD Gas	3.3	4.1	6.6
AAD Liq.	5.5	10.4	6.4
MxD Liq.	15.1	21.1	15.8

Table 4: Viscosity of some H₂S rich mixtures, comparison between experimental results [22], MD simulations and the proposed correlation. The compositions of the mixtures are given in mole percent of the individual compounds.

Gas n°	H ₂ S	CO ₂	N ₂	C1	C2	C3	IC4	NC4	IC5	NC5	C6	T(K)	P(MPa)	Exp η (cp)	MD η (cp)	Correlation η (cp)
11	22.6	0.5	0.46	75.61	0.71	0.06	0.02	0.02	0	0	0	352.55	34.47	0.03	0.032±0.001	0.032
13	49.35	3.08	2.66	44.47	0.23	0.06	0.02	0.03	0.02	0.01	0.03	322.05	17.24	0.03	0.036±0.001	0.036
14	70.03	8.65	0.92	20.24	0.16	0	0	0	0	0	0	352.55	9.4	0.022	0.022±0.001	0.021

Figures:

Figure 1:

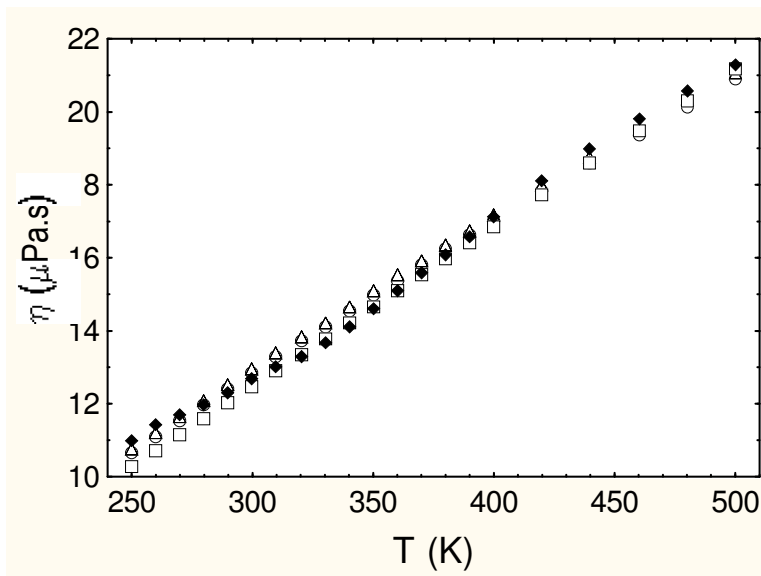


Figure 2:

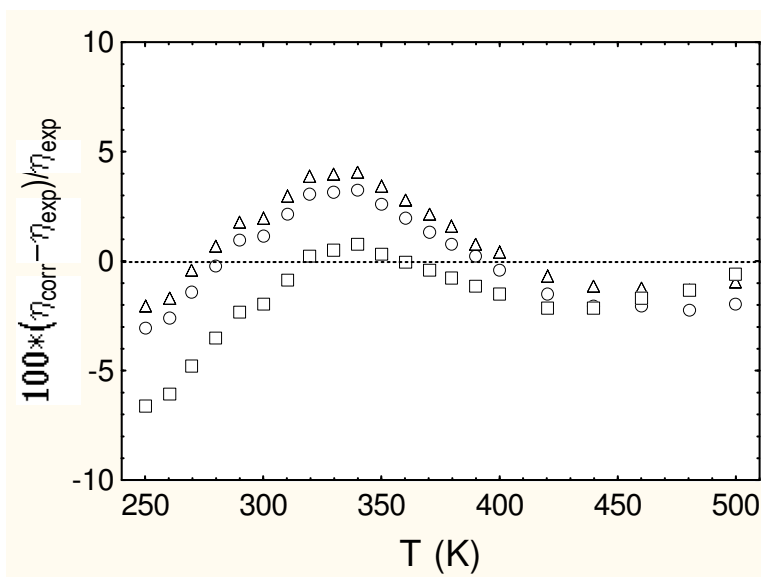


Figure 3:

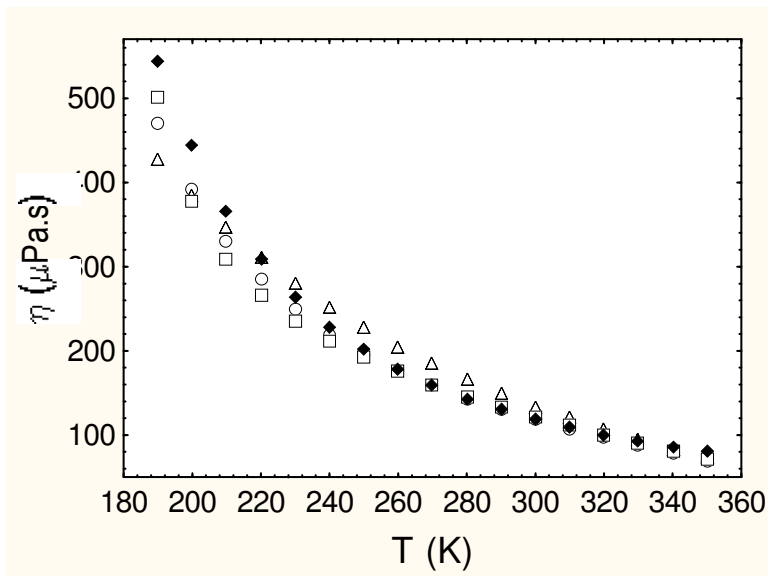


Figure 4:

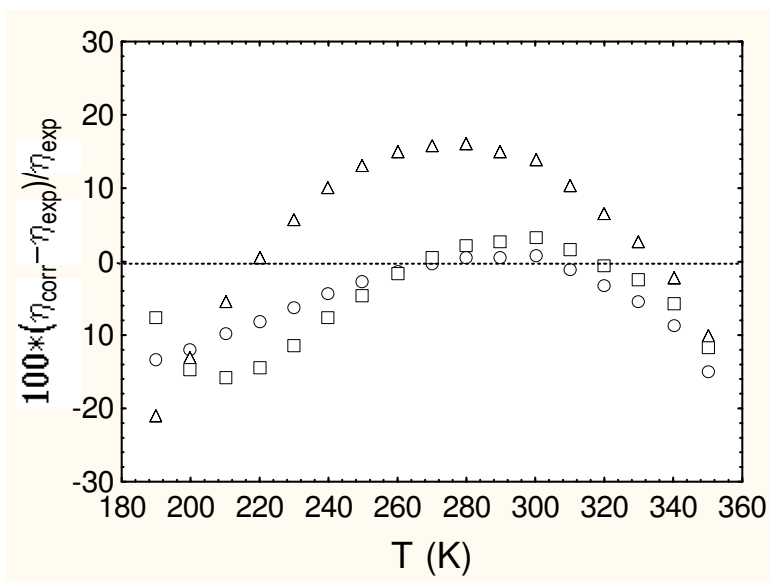


Figure 5:

