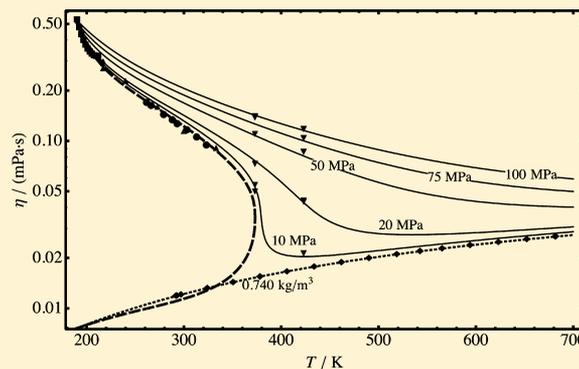


Reference Correlation for the Viscosity Surface of Hydrogen Sulfide

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ABSTRACT: Until recently, there was a substantial lack of reliable viscosity data for H₂S, making the regression of an accurate H₂S viscosity model significantly difficult. To derive a model for engineering applications (2008 H₂S model), a corresponding states approach that related molecules of similar shape to H₂S was applied to cover regions where no experimental data was available. Recently, new primary low-density experimental data and derived theoretical information have been published. Additionally, new high-pressure H₂S viscosity measurements [at (373.15 and 423.15) K and up to 100 MPa] have also been reported. Based on this, a new revised correlation for the viscosity of H₂S is presented in this work. The current correlation reproduces the primary H₂S viscosity data to within experimental uncertainty. The precision of the new correlation varies from reference quality (better than $\pm 0.20\%$) at low-densities to an estimated $\pm 5\%$ at 100 MPa and temperatures between (373 and 423) K. Outside this range of temperature there are no data to validate the accuracy of the model at elevated pressures; therefore we have conservatively estimated an uncertainty of roughly 10% in the low-temperature and high-density region ($T < 323$ K up to 100 MPa) and 5% for the high-temperature region ($T > 450$ K up to 100 MPa).



■ INTRODUCTION

As regulations become stricter for emissions of acid gases into the atmosphere and the penalty for violation increases, new and economical ways of reducing these emissions are becoming increasingly important to everyday operations. A viable sequestration option is the injection of these acid gases into formations for disposal and/or storage. Accurate viscosity data are required in the design of these injection schemes to ensure the projects are feasible and economically viable.

Recently, the friction theory (FT) for viscosity modeling^{1,2} has been used in an attempt to develop a reference model for the viscosity behavior of hydrogen sulfide³ (2008 H₂S FT model) as well as a simplified one-parameter FT viscosity model⁴ for engineering applications. The demand for viscosity models applicable to industrial schemes involving acid gases has also prompted the recent attention of various researchers into the development of other models.^{5,6}

During the development of the 2008 H₂S FT model, a literature review identified significant regions where additional data were needed to fill voids, resolve discrepancies of existing data sets, and cover regions where the available viscosity data was insufficient or inexistent. It became clear that new

experimental measurements or molecular simulation results were required to expand the available data set, particularly at low-density conditions as well as at conditions relevant to injection schemes.

Subsequent to the work leading to the 2008 H₂S FT model, three additional data sets have become available in the open literature within some of the critical areas originally identified. Giri et al.⁷ performed experimental H₂S viscosity measurements up to 100 MPa and temperatures of (373 and 423) K. The experiments were performed with a Cambridge EMV viscometer, and the authors estimated the uncertainty in the measurements to be (2 to 5)%.⁷ The second data set consisted of low-density measurements carried out with an all-quartz oscillating-disk viscometer with an estimated accuracy of better than 0.20%.⁸ The third data set consisted of ab initio molecular simulation results of the dilute gas limit covering a large range of temperatures (180 to 2000) K with a theoretical accuracy of $\pm (0.4$ to 1.0)%.⁹ These three data sets supplement the existing

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Table 1. Experimental and Simulation Data of the Viscosity of Hydrogen Sulfide in Addition to Schmidt et al. (2008)¹

author	year	no. points	T/K	pressure/density	method	fluid state	stated accuracy
Giri et al. ⁷	2012	25 ^a	373.2 to 423.2	(1 to 100) MPa	oscillating piston	supercritical	(2 to 5) %
Vogel ⁸	2010	35	291.6 to 682.0	0.740 kg·m ⁻³	oscillating-disk	vapor	0.2 %
Hellmann et al. ⁹	2012	equation	180 to 2000	zero density limit	<i>ab initio</i> molecular simulation	vapor	(0.4 to 1) %

^aExperimental work still ongoing; data presented at the Second International Acid Gas Injection Symposium.⁷

sets, for which a comprehensive review was presented by Schmidt et al.³ The new data sets are summarized in Table 1, and the additional experimental data provided by Giri et al.⁷ are presented in Table 2.

Table 2. Experimental Viscosities^a of H₂S⁷

373.15 K		423.15 K	
pressure	viscosity	pressure	viscosity
MPa	mPa·s	MPa	mPa·s
1.00	0.0159 ± 0.0005	1.01	0.0165 ± 0.0006
2.00	0.0145 ± 0.0005	1.01	0.0159 ± 0.0007
5.00	0.0159 ± 0.0005	2.01	0.0179 ± 0.0004
5.00	0.0162 ± 0.0007	5.00	0.0181 ± 0.0004
10.00	0.0483 ± 0.0014	5.01	0.0188 ± 0.0006
10.29	0.0537 ± 0.0018	10.00	0.0212 ± 0.0007
19.99	0.0722 ± 0.0025	19.99	0.0435 ± 0.0009
50.00	0.0970 ± 0.0025	20.00	0.0439 ± 0.0010
99.61	0.1369 ± 0.0029	50.00	0.0849 ± 0.0018
100.25	0.1390 ± 0.0032	50.01	0.0858 ± 0.0018
100.44	0.1380 ± 0.0032	75.00	0.1033 ± 0.0021

^aThe accuracy of temperature and pressure is ± 0.02 K and ± 0.03 MPa, respectively, with a confidence interval of 0.995.

It should be underlined that a major region lacking reliable data was, unquestionably, the low-density region. Although for many oil industry applications the low-density behavior of some thermophysical properties is frequently neglected, as it is far from operating conditions, this is not the case for applications including H₂S. In general, along isotherms close to the critical temperature, a fluid viscosity will strongly depend on its initial density dependency (second viscosity virial coefficient) and will sharply increase as a function of density or pressure (e.g., see Figures 5 and 6 in ref 2); thus, for near critical temperatures the viscosity initial density dependency must be well-described. The critical temperature of H₂S is 373.1 K, which is well within the conditions of many injection well tubulars and surface compression systems. In the 2008 H₂S model³ the low-density region was perhaps the weakest area of the model. This area could not be covered by our approach as the FT does not strictly apply to this region. Fortunately, the recent low-density measurements of Vogel,⁸ combined with dilute gas limit molecular simulation results of Hellman et al.,⁹ have, for the first time, provided reference quality data in the low-density viscosity region of H₂S covering practically all temperature ranges of interest.

It should also be mentioned that the 2008 H₂S FT model was built using a corresponding states approach based on a scaled database of molecules having similar shapes or behavior as H₂S. This scaling procedure was performed to supplement the lack of experimental data. The new available data at elevated pressures are in the range of some of the scaled data that were used in the 2008 model. In fact, the 2008 model agreed with the new data to within the experimental uncertainty. The main

difference between the new model and the previous 2008 H₂S FT model is in the low-density region, where the new available measurements and simulation results are of reference quality. The newly published low-density data depart substantially from the data previously available in this region. The previous data were measured at 0.1 MPa and were considered primary data sets for the 2008. However, the variability in those data sets and the significant departure from the new dilute region data sets resulted in the 0.1 MPa data set to not be considered further in the development of this model. Thus, the improvement in the model is mainly due to the new information found in the recent publication of reference data for gaseous H₂S by Vogel⁸ and Hellmann et al.⁹

■ THE H₂S GFT REFERENCE MODEL FORMULATION

The generalized friction theory (GFT) approach proposed by Quiñones-Cisneros and Deiters² has been applied for the development of the reference viscosity model of H₂S. In general terms, a GFT model can be written as follows:

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

where η_0 corresponds to the dilute-gas limit, η_i is the initial density dependency, and η_f is a residual friction viscosity term. The η_f term is built upon a balance between repulsive pressure (p_r) and attractive pressure (p_a) contributions to the isotropic pressure (p). In the GFT approach, this is achieved by making use of the internal pressure (π_T) concept according to the following definitions:

$$p_a = -\pi_T \quad (2)$$

and

$$p_r = p - p_a = T \left(\frac{\partial p}{\partial T} \right)_v \quad (3)$$

For the calculation of p_a and p_r , a reference equation of state (EoS) is required, and the Lemmon and Span¹⁰ short reference equation of state for H₂S was selected.

As discussed in the original GFT work,² for an accurate description of the low-density viscosity behavior, a separation of the repulsive pressure contribution into the linear ideal gas term (p_{id}) and a residual higher order term (Δp_r) is recommended:

$$p_r = p_{id} + \Delta p_r \quad (4)$$

The ideal gas term, p_{id} , provides the linear initial density–viscosity dependence responsible for the second viscosity virial coefficient (B_η). The separation introduced in eq 4 removes the linear density term η_i from η_f . This work uses η_i as calculated from Vogel.⁸

The final GFT full model which was implemented is a simplification of the GFT model originally used for water and carbon dioxide:²

$$\eta_f = \kappa_a p_a + \kappa_r \Delta p_r + \kappa_{aa} p_a^2 + \kappa_{rr} p_r^2 \quad (5)$$

In eq 5 the friction parameters (κ_a , κ_r , κ_{aa} , κ_{rr}) are only temperature-dependent, and a full discussion of their physical meaning is found elsewhere.²

Dilute Gas Limit. Until recently, one of the major limitations in describing the viscosity surface for H₂S had been the lack of reliable information for the zero density limit region, which is now covered by the ab initio potential correlation of Hellmann et al.⁹ This correlation has the following formulation:

$$\frac{\eta_0}{\mu/\text{Pa}\cdot\text{s}} = 8.7721 \frac{\sqrt{T/\text{K}}}{S_\eta^*(T^*)} \quad (6)$$

where the reduced effective cross section, $S_\eta^*(T^*)$, is given by

$$S_\eta^*(T^*) = \sum_{i=0}^5 \frac{\alpha_i}{T^{*i}} \quad (7)$$

with $T^* = T/T_{\text{ref}}$ and $T_{\text{ref}} = 276$ K. The values for the coefficients α_i are reproduced from Hellmann et al.⁹ in Table 3.

Table 3. Hydrogen Sulfide Parameters for the Dilute Gas Limit Model of Hellmann et al.⁹ and Second Viscosity Virial Coefficient of Vogel et al.¹¹

<i>i</i>	α_i	β_i
0	0.53242	-19.572881
1	0.93715	219.73999
2	-0.69339	-1015.3226
3	1.16432	2471.01251
4	-0.84306	-3375.1717
5	0.20534	2491.6597
6		-787.26086
7		14.085455
8		-0.34664158

Initial Density Dependency. The recent low-density measurements of Vogel⁸ cover the temperature range of (290 to 600) K at a fixed density of 0.740 kg·m⁻³ (experimental uncertainty of 0.2 %); Vogel⁸ also reports a model for the second viscosity virial coefficient of H₂S. The viscosity virial coefficient is particularly relevant due to the fact that it is a derived property and because the Vogel⁸ data (considered to be a primary data set) was at only one density value. It is not possible to obtain a reliable derivation of the kinematic viscosity initial density dependency based solely on a single density point. Vogel identified the same problem and, after analyzing the available experimental and theoretical data (the same data considered in this work), recommended the use of a previously derived empirical equation for the second viscosity virial coefficient, B_{η} ¹¹ after the Rainwater–Friend theory.¹² Vogel's empirical model for B_{η}^* is given by:

$$B_{\eta}^* = \frac{B_{\eta}}{N_A \sigma^3} = \sum_{i=0}^6 \beta_i T_r^{-0.25i} + \beta_7 T_r^{-2.5} + \beta_8 T_r^{-5.5} \quad (8)$$

In Vogel's model, T_r is the reduced temperature,

$$T_r = \frac{k_B T}{\epsilon} \quad (9)$$

where N_A and k_B are the Avogadro's and Boltzmann's constants, respectively. The constants σ and ϵ/k_B are the Lennard–Jones 12-6 potential parameters, which in the case of hydrogen sulfide are estimated as 0.3565 nm and 355.8 K, respectively. For completeness, the coefficients β_i in eq 8 are also listed in Table 3.¹¹

In terms of B_{η} , η_i is readily given by the following expression linear in density:

$$\eta_i = \eta_0 B_{\eta} \rho \quad (10)$$

where η_0 is calculated using eq 6.

Friction Term. The mathematical form for the temperature-dependent friction coefficients in eq 5 is essentially similar to that originally proposed:²

$$\kappa_a = (a_0 + a_1 \psi_1 + a_2 \psi_2) T_c / T \quad (11)$$

$$\kappa_r = (b_0 + b_1 \psi_1 + b_2 \psi_2) T_c / T \quad (12)$$

$$\kappa_{aa} = (A_0 + A_1 \psi_1 + A_2 \psi_2) T_c / T \quad (13)$$

$$\kappa_{rr} = (B_0 + B_1 \psi_1 + B_2 \psi_2) T_c / T \quad (14)$$

where

$$\psi_1 = \exp[T_c / T] \quad (15)$$

and

$$\psi_2 = \exp[(T_c / T)^2] \quad (16)$$

with $T_c = 373.1$ K.¹⁰

RESULTS

A comparison between the new high-pressure measurements of Giri et al.⁷ and the 2008 H₂S FT model shows that the original model actually reproduces the new measurements to within the experimental uncertainty. These results validate the approach originally used in the derivation of the 2008 H₂S FT model. The low-density region of high-uncertainty has now been better described with the present model. The parameters in eqs 11 to 14 have been optimized by linear regression using the same database as in Schmidt et al.³ (excluding the low-density 2008 estimations), the dilute gas limit model of Hellmann et al.,⁹ the second viscosity virial coefficient model and low-density data of Vogel,⁸ and the new measurements by Giri et al.⁷ The regressed parameters results for the GFT model are reported in Table 4.

Figure 1 shows a comparison between the 2008 H₂S FT model and the new model, along with the recent data of Giri et

Table 4. Hydrogen Sulfide Reference Friction Theory Model Parameters

<i>i</i>	a_i mPa·s·bar ⁻¹	b_i mPa·s·bar ⁻¹	A_i mPa·s·bar ⁻²	B_i mPa·s·bar ⁻²
0	68.9659·10 ⁻⁶	153.406·10 ⁻⁶	0.782380·10 ⁻⁹	-9.75792·10 ⁻⁹
1	-22.0494·10 ⁻⁶	8.45198·10 ⁻⁶	-0.64717·10 ⁻⁹	-3.19303·10 ⁻⁹
2	-42.6126·10 ⁻⁶	-113.967·10 ⁻⁶	1.39066·10 ⁻⁹	12.4263·10 ⁻⁹

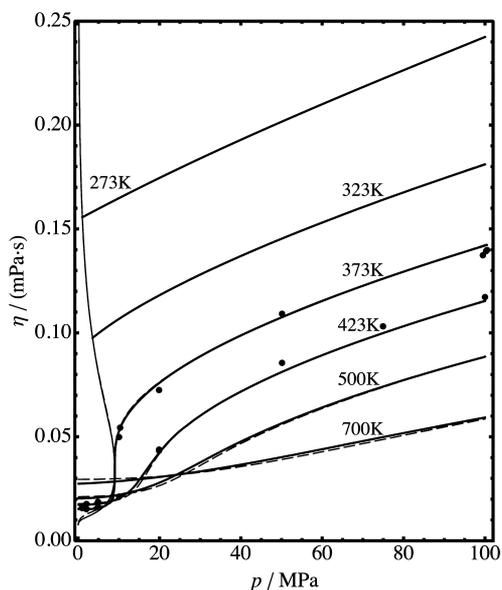


Figure 1. Viscosity vs pressure comparison between the 2008 H₂S Schmidt et al.³ model (---) and this work model (—) along with the high-pressure data of Giri et al.⁷ (●).

al.⁷ The figure shows that both models deliver similar results at elevated pressures and a good representation of the new high-pressure measurements. The main deficiencies of the 2008 H₂S FT model in the low-density area have already been discussed by Vogel,⁸ as depicted in Figure 2; however, the new model reproduces the new measurements of Vogel within the reported experimental uncertainty.

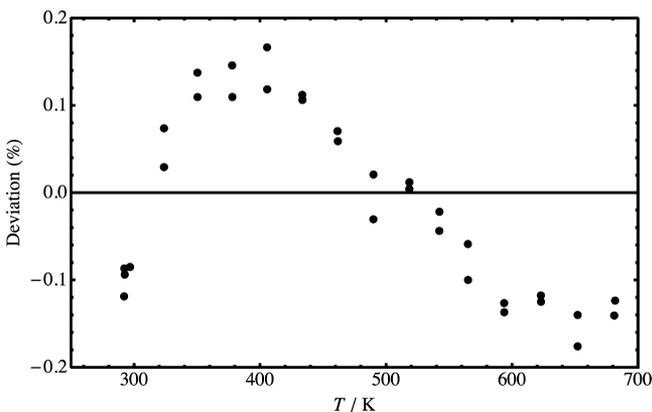


Figure 2. Viscosity deviation vs temperature for the low-density primary data of Vogel.⁸

Figure 3 shows the viscosity versus temperature performance for selected isobars as well as the isochore corresponding to the low-density measurements of Vogel⁸ along with the other data considered to be primary. To avoid confusion, in the case of Giri et al.⁷ only their data close to the isobars depicted in Figure 3 are shown. Similar to the 2008 model, with the exception of the high-pressure measurements of Giri et al.⁷ there is an obvious lack of dense phase-viscosity measurements for H₂S. Yet, it should be noted that the new high-pressure data of Giri et al.⁷ are near the critical isotherm, where a sharp increase in the viscosity surface with pressure is evident. Therefore, it is remarkable that the data from Giri et al.⁷ are actually predicted by the 2008 model to within the reported experimental

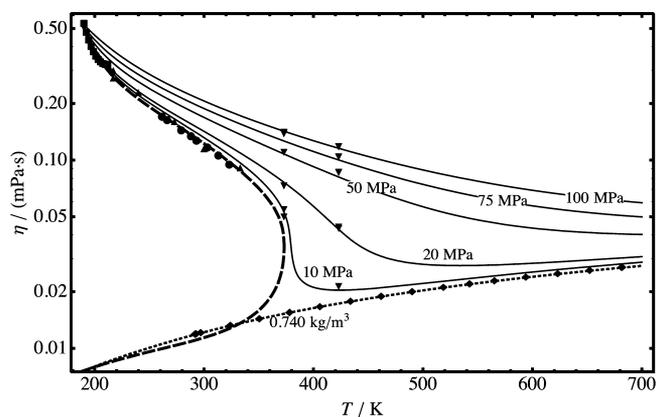


Figure 3. This work reference H₂S viscosity model performance depicting the (10, 20, 50, 75, and 100) MPa isobars (—), the phase boundary (---), and the 0.740 kg·m⁻³ isochore (.....). □, Vogel;⁸ ▼, Giri et al.;⁷ ●, Hennel and Krynicki;¹³ ■, Runnovskaya et al.;¹⁴ and ▲, molecular dynamics simulation results of Nieto-Draghi et al.¹⁵

uncertainty. This result validates the original approach used by Schmidt et al.³ in the derivation of the 2008 H₂S FT model, and it is expected that, away from the critical isotherm, the same or even better performance would be delivered.

Table 5 shows the deviation results for the H₂S primary data, where the absolute average deviation (AAD) and bias are defined as follows:

$$\text{AAD} = 100 \cdot \frac{1}{n} \sum_{i=1}^n \left| \frac{\eta_{i,\text{calcd}} - \eta_{i,\text{exptl}}}{\eta_{i,\text{exptl}}} \right| \quad (17)$$

and

$$\text{bias} = 100 \cdot \frac{1}{n} \sum_{i=1}^n \left(\frac{\eta_{i,\text{calcd}} - \eta_{i,\text{exptl}}}{\eta_{i,\text{exptl}}} \right) \quad (18)$$

CONCLUSIONS

The optimal design of an acid-gas injection scheme requires various physical properties. Particularly for large injection schemes, the viscosity is important to establish the optimum pipeline diameter for the transport of the acid gas from the compressor to the injection well and for estimating the pressure loss due to fluid friction in the wellbore. The viscosity is also an important parameter for performing reservoir simulations.

An updated literature review was described and used to develop an updated H₂S reference viscosity model. Further experimental measurements or molecular simulations are required to expand the data set, not only for pure H₂S but for mixtures found in sour gas treating and acid gas injection applications. Although the rather accurate prediction made by the 2008 H₂S FT model of the new measurements by Giri et al.⁷ is encouraging, outside of these two isotherms at (373.15 and 423.15) K and the saturation liquid region, there are practically no published H₂S measurements for the dense phase; therefore, the region of dense-fluid viscosity of H₂S remains an area of opportunity for future research.

The model presented in this work is intended to provide reasonable estimations for the H₂S viscosity surface. The model accuracy goes from reference precision at low-density (better than 0.2 %) to reasonable engineering uncertainty of around 5 % at elevated pressures to 100 MPa and temperatures between

Table 5. Comparison of the Friction Theory Model Results and the Primary Data

author	temperature range/K	pressure or density range	uncertainty/%	AAD/%	bias/%	no. points
Hennel and Krynicki ¹³	261.7 to 323.2	saturation	4	2.71	2.71	8
Runnovskaya et al. ¹⁴	190.1 to 211.8	saturation	5 ^a	3.20	0.01	11
molecular simulation: Nieto-Draghi et al. ¹⁵	217.2 to 333.2	saturation	10–15	4.76	–1.84	6
Giri et al. ⁷	373 to 423	(1 to 100) MPa	2 to 5	3.12	–1.01	25
Vogel ⁸	292 to 682	0.749 kg·m ^{–3}	0.02	0.09	–0.01	32

^aNot given, estimated.

(373 and 423) K. The model accuracy may deteriorate [to ranges of (10 to 15) %] outside the range validated by the measurements, particularly at elevated pressures of 100 MPa and temperatures below 373.15 K. At temperatures above 423 K the deviations are expected to be better than 10 %, but there are no data to validate such estimation.

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Notes

The authors declare no competing financial interest.

REFERENCES

- Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Stenby, E. H. The Friction Theory (*f*-theory) for Viscosity Modeling. *Fluid Phase Equilib.* **2000**, *169*, 249–276.
- Quiñones-Cisneros, S. E.; Deiters, U. K. Generalization of the Friction Theory for Viscosity Modeling. *J. Phys. Chem. B* **2006**, *110*, 12820–12834.
- Schmidt, K. A. G.; Quiñones-Cisneros, S. E.; Carroll, J. J.; Kvamme, B. Hydrogen Sulfide Viscosity Modeling. *Energy Fuels* **2008**, *22*, 3424–3434.
- Quiñones-Cisneros, S. E.; Zéberg-Mikkelsen, C. K.; Stenby, E. H. One Parameter Friction Theory Models for Viscosity. *Fluid Phase Equilib.* **2001**, *178*, 1–16.
- Galliero, G.; Boned, C. Dynamic viscosity estimation of hydrogen sulfide using a predictive scheme based on molecular dynamics. *Fluid Phase Equilib.* **2008**, *269*, 19–24.
- Motahhari, H.; Satyro, M. A.; Yarranton, H. W. Viscosity prediction for natural gas processing appl. *Fluid Phase Equilib.* **2012**, *322–323* (1), 56–65.
- Giri, B. R.; Blais, P.; Marriott, R. A. Viscosity and Density Measurements for Sour Gas Fluids at High Temperatures and Pressures. In *Carbon Dioxide Sequestration and Related Technologies*, Wu, Y., Carroll, J. J., Du, Z., Eds.; John Wiley & Sons: Salem, MA, 2011.
- Vogel, E. Reference Viscosities of Gaseous Methane and Hydrogen Sulfide at Low Density in the Temperature Range from (292 to 682) K. *J. Chem. Eng. Data* **2011**, *56*, 3265–3272.
- Hellmann, R.; Bich, E.; Vogel, E.; Vesovic, V. The Thermophysical Properties of Dilute Hydrogen Sulfide Gas. *J. Chem. Eng. Data* **2012**, *57*, 1312–1317.
- Lemmon, E. W.; Span, R. Short Fundamental Equations of State for 20 Industrial Fluids. *J. Chem. Eng. Data* **2006**, *51*, 785–850.

(11) Vogel, E.; Küchenmeister, C.; Bich, E.; Laesecke, A. Reference Correlation of the Viscosity of Propane. *J. Phys. Chem. Ref. Data* **1998**, *27*, 947–970.

(12) Rainwater, J. C.; Friend, D. G. Second viscosity and thermal-conductivity virial coefficients of gases: extension to low reduced temperature. *Phys. Rev. A* **1987**, *36*, 4062–4066.

(13) Hennel, J. W.; Krynicki, K. Viscosity of Liquid Hydrogen Sulfide. *Acta Phys. Pol.* **1959**, *18*, 523–526.

(14) Runnovskaya, I. V.; Zorin, A. D.; Devyatikh, G. G. Viscosity of Condensed Volatile Inorganic Hydrides of Group III-VI Elements. *Russ. J. Inorg. Chem.* **1970**, *15*, 1338–1339.

(15) Nieto-Draghi, C.; Mackie, A. D.; Bonet-Avalos, J. Transport coefficients and dynamic properties of hydrogen sulfide from molecular simulation. *J. Chem. Phys.* **2005**, *123*, 014505 (1–8).