CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

Chief Editors: Sauro Pierucci, Jiří J. Klemeš
Copyright © 2013, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-23-5; **ISSN** 1974-9791

A publication of
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1332263

Viscosity Modelling of Reservoir Fluids over Wide Temperature and Pressure Ranges

Ricardo Macías-Salinas*[a], Marco A. Aquino-Olivos[b], Fernando García-Sánchez[c]

[a]ESIQIE-Departamento de Ingeniería Química, Instituto Politécnico Nacional, Zacatenco, México, D.F. 07738
[b]Programa de Aseguramiento de Recuperación de Hidrocarburos, Instituto Mexicano del Petróleo, Eje Central Lázaro Cardenas 152, México, D.F. 07730
[c]Laboratorio de Termodinámica, Programa de Investigación en Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cardenas 152, México, D.F. 07730
rms@ipn.mx

A previously developed viscosity model based on the Significant Structure Theory (Cruz-Reyes et al., 2005) was modified for the accurate correlation and/or prediction of viscosity of reservoir fluids varying from low to high molar masses and over wide temperature and pressure ranges; 65-1,300 K, and 1-1,000 bar, respectively. Viscosity modeling was conducted for typical reservoir fluids including N_2, CO_2, H_2S, C_1, C_2, C_3, iC_4, C_4, and from C_5 to C_{18}. The viscosity modeling performance of the present approach was assessed during the representation of experimental viscosities of the aforementioned reservoir fluids obtaining highly satisfactory results.

1. Introduction

Viscosity is a key transport property involved in process design and development, as well as reservoir simulation; its accurate knowledge is therefore paramount. For computer simulations there is still a need to develop reliable and yet simple models for the correlation and/or prediction of viscosities of pure fluids within wide ranges of temperature and pressure. A significant amount of modelling works has so far published in the literature dealing with the viscosity of pure fluids at different temperature and pressure conditions. A detailed analysis of these works reveals that the majority of the viscosity models range from semi-theoretical to purely empirical. These works also reveal that the Chapman-Enskog theory, the corresponding-states principle, and the Eyring's chemical kinetics-based theory stand as the most popular and utilized approaches in the viscosity modeling of pure substances. Many of these works are applicable only to some specific phases (either gas or liquid), and were developed and validated on pure hydrocarbons and light petroleum fluids. Some other viscosity models are indeed applicable to both gas and liquid phases (Guo et al., 2001; Quiñones-Cisneros et al., 2000; Quiñones-Cisneros and Dieters, 2006), however, either they are cumbersome to use or their range of applicability is limited. The purpose of the present work is thus to develop a simple yet accurate viscosity model for reservoir fluids having in mind that (1) it should be applicable to the gas and liquid phases over wide ranges of temperature and pressure (encompassing the zero-density limit, the high-density region, and the vicinity of the critical point), (2) it should be able to handle petroleum fluids ranging from low to high molar masses, and (3) it should be computationally efficient so it can be further incorporated into a reservoir simulator.

2. Modelling Approach

The present modelling work is based on a previously developed viscosity model (Cruz-Reyes et al., 2005) based on the Significant Structure Theory (SST) originally proposed by Eyring et al. (1958). The SST visualizes a liquid as having both "solid-like" and "gas-like" degrees of freedom with "fluidized vacancies" of molecular size randomly distributed throughout a quasi-lattice structure. A molecule displays gas-like behavior when it jumps from one vacant site to another. The vacant sites are assumed to have molecular size and to

Please cite this article as: Macias-Salinas R., Aquino-Olivos M.A., Garcia-Sánchez F., 2013, Viscosity modeling of reservoir fluids over wide temperature and pressure ranges, Chemical Engineering Transactions, 32, 1573-1578 DOI: 10.3303/CET1332263

move freely through the lattice. On the other hand, when a molecule remains on its site, for the time it acquires solid-like properties. If V and V_s are the molar volumes of the fluid and solid phases, respectively, thus the difference V-V_s stands for the number of vacancies (or the number of gas-like molecules). Assuming that both occupied and vacant sites are randomly distributed, the fraction of gas-like molecules is,

$$x_g = \frac{V - V_s}{V} \tag{1}$$

while the fraction of solid-like molecules is given by

$$x_s = 1 - x_g = \frac{V_s}{V} \tag{2}$$

In this context, the viscosity of a liquid is calculated from two main components: a gas-like (η_g) and a solid-like (η_s) contribution as follows,

$$\eta = x_g \cdot \eta_g + x_s \cdot \eta_s \tag{3}$$

2.1 Gas-Like Contribution

The equations of Chung et al. (1988), based on the kinetic theory of Chapman-Enskog, were used here to calculate the viscosity of the gas-like molecules. The method of Chung et al. (1988) applies in the limit of dilute gas for non-polar and polar fluids within a wide range of temperatures. The equations of Chung et al. are given below,

$$\eta_g = 40.785 \frac{\sqrt{M \cdot T}}{V_c^{2/3} \Omega^*} \cdot F_c \quad [=]\ \mu\text{P} \tag{4}$$

$$\Omega^* = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.43787T^*)} \\ - 6.435 \times 10^{-4} (T^*)^{0.14874} \sin\left[18.0323 (T^*)^{-0.7683} - 7.27371\right] \tag{5}$$

with

$$T^* = 1.2593 \cdot T / T_c \quad \text{and} \quad F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \tag{6a, 6b}$$

The factor F_c in Eq. (6b) serves to account for molecular shapes and polarities of dilute gases where ω is the acentric factor, μ_r is a dimensionless dipole moment (greater than zero for polar substances), and κ is a correction factor for the hydrogen bonding effect of associating substances. Values of κ have been given by Chung et al. (1988).

2.2 Liquid-Like Contribution

Cruz-Reyes et al. (2005), in their model for the simultaneous correlation of saturated viscosities of pure gases and liquids, utilized the viscosity model for saturated liquids by Macías-Salinas et al. (2003) as the framework to calculate the viscosity of the solid-like molecules. Accordingly, the expression for η_s proposed by Cruz-Reyes et al. (2005) is based on the Eyring's absolute rate theory and is given by

$$\eta_s = \frac{RT}{V - V_s} \cdot \frac{1}{\gamma} \exp\left[\alpha \left(\frac{\Delta U_{vap}}{RT}\right)^{\beta}\right] \exp(Z) \tag{7}$$

where γ represents the frequency of a molecule that jumps from its initial position to a vacant site, while α and β are two adjustable constants used in the power-law expression between the activation energy, and the internal energy of vaporization ΔU_{vap}; the other variables, V and Z are the molar volume and the compressibility factor of the fluid, respectively, at the temperature and pressure of saturation. Rather than assuming a constant value for the "jumping" frequency γ, Cruz-Reyes et al. (2005) made this parameter dependent on the number of vacancies as follows:

$$\gamma = 10^{12} \cdot \gamma_0 \cdot x_g^{-1} \tag{8}$$

where γ_0 is an adjustable parameter and x_g is given in Eq. (1). In this work, Eq. (7) was modified to extend its applicability over much wider ranges of temperature and pressure (and not only along the saturation line). First of all, the jumping frequency γ was also found to vary with pressure as follows:

$$\gamma = 10^{12} \cdot x_g^{-1} \cdot \left(\gamma_0 + \gamma_1 P\right) \tag{9}$$

where γ_0 and γ_1 are two adjustable parameters. Second, the activation energy for the viscous flow was assumed to be negatively proportional to the residual internal energy of the fluid of interest at given temperature and pressure, that is:

$$\Delta G^{\neq} = -\alpha \cdot \Delta U^r(T,P) \tag{9}$$

where α is the proportionality factor. Finally, we found that the second exponential term in Eq. (7) becomes more predominant at elevated pressures; accordingly, a power-law expression for Z was adopted here to properly capture the high-pressure effect on the η_s value. Based on the aforementioned modifications, the final expression to calculate the viscosity of the solid-like molecules is therefore given by:

$$\eta_s = \frac{RT}{V} \cdot \frac{1}{10^{12} \cdot \left(\gamma_0 + \gamma_1 P\right)} \exp\left[-\alpha \frac{\Delta U^r}{RT}\right] \exp\left(\beta_0 Z^{\beta_1}\right) \tag{10}$$

As in Cruz-Reyes et al. (2005), we also used two simple cubic equations of state (CEoS): Soave-Redlich-Kwong (Soave, 1972), and Peng-Robinson (Peng and Robinson, 1976) to compute the thermodynamic properties (V, ΔU^r and Z) required in Eqs. (1), (2), and (10). Another important property needed by the model is the molar volume of the solid at the melting point V_s. This quantity was also conveniently estimated from the CEoS as close-packed by the following approximation:

$$V_s \approx b \tag{11}$$

where b is the van der Waals co-volume; its value depends on the CEoS chosen.

3. Results and Discussion

The present modeling approach was first applied to the correlation of experimental viscosities of selected reservoir fluids within wide temperature and pressure ranges (covering the low- and high-density regions). The chosen reservoir fluids were Nitrogen, CO_2, H_2S, Methane, Ethane, Propane, n-Butane, i-Butane, n-Pentane, n-Hexane, n-Decane, n-Dodecane, and n-Octadecane. A least-square fit based on the Levenberg-Marquadt method was then performed to obtain the model parameters, namely γ_0, γ_1, α, β_0, and β_1. The minimization of the following objective function served for this purpose:

$$\min f = \sum_{j=1}^{N} \left[1 - \eta_j^{\mathrm{cal}} / \eta_j^{\mathrm{exp}}\right]^2 \tag{12}$$

where N is the number of experimental points, whereas η^{exp} and η^{cal} stand for the observed and calculated viscosities, respectively. Table 1 lists the corresponding correlating results obtained for the 13 reservoir fluids considered in this work. This table includes, for each reservoir fluid, the number of experimental points, the temperature range, the pressure range, the source(s) of experimental viscosity data, and the resulting percent of absolute average deviations (*AAD*) between experimental and calculated viscosities using both CEoS. As seen in this table, experimental data cover, overall speaking, a wide temperature range (65-1,300 K), and a wide pressure range (1-1,000 bar). Table 1 shows that the ability of the present approach in representing the experimental viscosity data is quite good with overall *AAD* values of 2.23% using the SRK CEoS, and 2.11% using the PR CEoS based on a total of 7,043 data points. As a matter of fact, for each reservoir fluid, both CEoS give comparable results, however, the PR CEoS yields slightly lower *AAD* values in all cases (very likely because the PR CEoS yields better volumetric estimations in the liquid phase). Furthermore, the largest *AAD* values were obtained for n-Butane (3.8% using the SRK CEoS, and 3.43% using the PR CEoS) whereas the lowest *AAD* values were obtained for n-Dodecane (0.67% using the SRK CEoS, and 0.63% using the PR CEoS).

Table 1: Reservoir fluids considered in this work & model performance (AAD values)

Component	***N***	***T, K***	***P, bar***	***Source(s)***	***% AAD SRK***	***% AAD PR***
Nitrogen	1,143	65 – 1,300	1 – 1,000	Stephan & Lucas (1979)	2.58	2.54
CO_2	497	310 – 900	1 – 1,000	Stephan & Lucas (1979)	1.39	1.28
H_2S	878	340 – 760	1 – 1,000	NIST Webbook (2009)	1.30	1.14
Methane	590	100 – 520	1 – 700	Stephan & Lucas (1979)	2.70	2.63
Ethane	665	320 – 750	1 – 700	Stephan & Lucas (1979)	1.75	1.58
Propane	677	175 – 750	1 – 1,000	Stephan & Lucas (1979) Vogel et al. (1998)	2.65	2.57
n-Butane	576	280 – 850	1 – 700	Stephan & Lucas (1979)	3.80	3.43
i-Butane	658	310 – 850	1 – 500	Stephan & Lucas (1979)	3.05	3.02
n-Pentane	438	320 – 900	1 – 500	Stephan & Lucas (1979)	1.85	1.62
n-Hexane	392	380 – 1,000	1 – 500	Stephan & Lucas (1979)	1.87	1.78
n-Decane	292	280 – 520	1 – 1,000	Stephan & Lucas (1979) Ducoulombier et al. (1986)	1.57	1.48
n-Dodecane	206	300 – 520	1 – 500	Stephan & Lucas (1979)	0.67	0.63
n-Octadecane	22	313.2 – 373.2	1 – 1,000	Ducoulombier et al. (1986)	1.98	1.96
OVERALL	**7,034**	**...**	**...**	**...**	**2.23**	**2.11**

Example correlating results are graphically shown for Methane, CO_2, H_2S, Propane, n-Dodecane, and n-Octadecane in Figures 1 through 4. As shown by Figure 1, the present SST-based model does a pretty good job in representing the four experimental viscosity isotherms of Methane and CO_2, particularly the isotherm near the critical point of the fluid (200 K for Methane, 310 K for CO_2) for which the model captures remarkably well the rapid viscosity change with pressure across the critical pressure (P_c). Hydrogen sulfide (H_2S) is quite an interesting reservoir fluid since it is the only highly polar and associating oil constituent for which experimental viscosity data is scarce. Due to the limited availability of experimental viscosity data for H_2S, we used the on-line software package called NIST Chemistry Webbook (REFPROP 7, Lemmon et al., 2005) as a reference to model the viscosity of pure H_2S. As shown in Table 1, the performance of the present approach is quite good in representing the reference viscosity data within wide ranges of temperature and pressure with low *AAD* values (1.3% using SRK, 1.14% using PR).

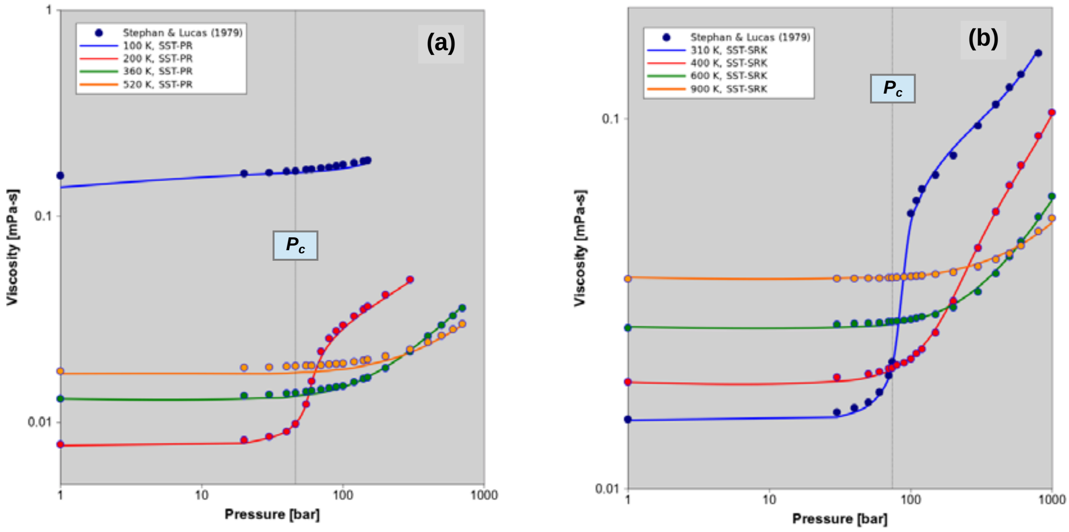

Figure 1: Correlated viscosities using the present approach: (a) Methane, (b) CO_2

Figure 2a compares the results delivered by the present model to the NIST package of thermophysical properties for four selected isotherms; the resulting agreement looks rather well. Very recently, Giri et al. (2012) performed experimental H_2S viscosity measurements at supercritical conditions up to 1,000 bar, and temperatures of 373 and 423 K. In order to verify the suitability of the chosen reference viscosity data for H_2S, and the present regressed model parameters, we tested the predictive capabilities of our model against the experimental viscosity data of Giri et al. (2012). As shown by Figure 2b, the present model (using the SST-PR version) yields reasonable viscosity predictions for the two isotherms, particularly for the isotherm at 423 K. Further, as depicted by Figures 3a and 3b, the present approach also provides a very good fit to experimental viscosities of Propane (a low molar mass hydrocarbon), and n-Dodecane (a high molar mass hydrocarbon). For the particular case of Propane, its viscosities measured by two different authors (Stephan and Lucas, 1979; Vogel et al., 1998) are well represented by the present SST-PR model.

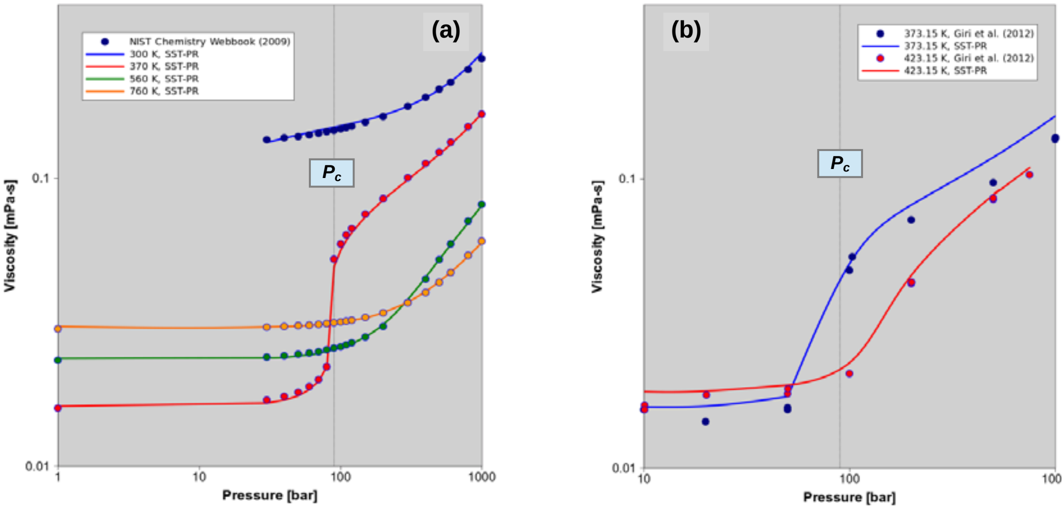

Figure 2: Model performance during the (a) correlation of H_2S viscosity, and (b) prediction of H_2S viscosity

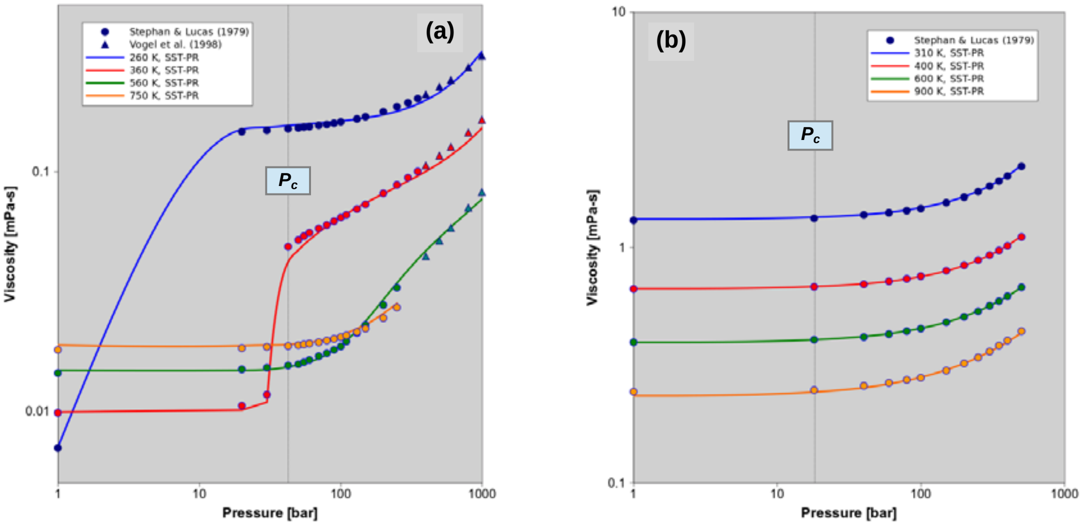

Figure 3: Correlated viscosities using the present approach: (a) Propane, (b) n-Dodecane

Figure 4a confirms the predictive capabilities of the present model in representing well the experimental viscosities of n-Dodecane at elevated pressures (up to 2,000 bar); that is, at pressures beyond the maximum correlating pressure considered here (500 bar). Finally, as shown by Figure 4b, the performance of the present SST-based model in correlating the experimental viscosity of the reservoir fluid with the highest molar mass considered here (n-Octadecane) was also highly satisfactory.

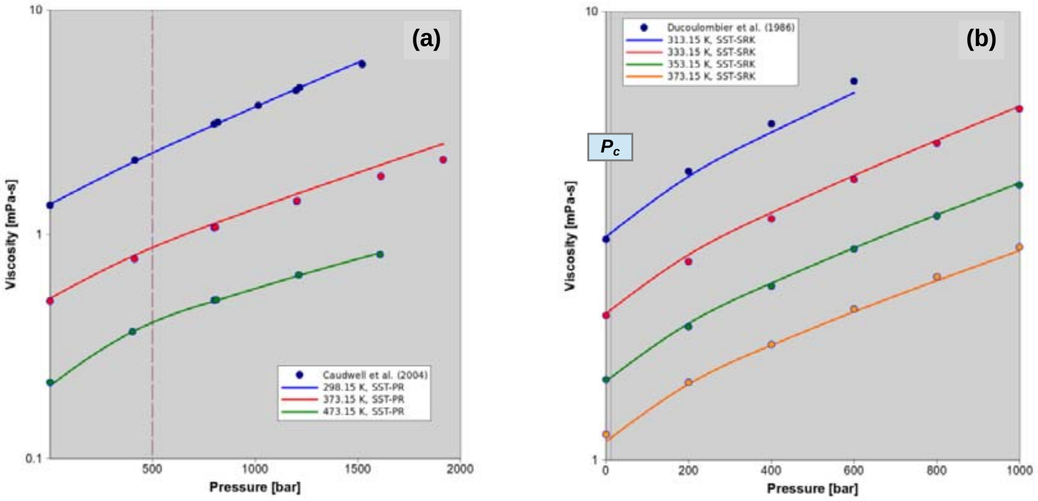

Figure 4: Model performance during the (a) prediction of C_{12} viscosity, and (b) correlation of C_{18} viscosity

Conclusions

A versatile viscosity model based on the Significant Structure Theory was developed here for the accurate correlation and/or prediction of viscosity of reservoir fluids varying from low to high molar masses and over wide temperature and pressure ranges. The performance of the present modelling approach was highly satisfactory during the representation of experimental viscosity data of all the reservoir fluids considered in this work.

References

Caudwell, D.R., Trusler, J.P.M., Vesovic, V., Wakeman, W.A., 2004, The Viscosity and Density of n-Dodecane and n-Octadecane at Pressures up to 200 MPa and Temperatures up to 473 K. Int. J. Thermophysics, 25, 1339.

Chung, T.-H., Ajlan, M., Lee, L.L., Starling, K.E., 1988, Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties. Ind. Eng. Chem. Res., 27, 671.

Cruz-Reyes, G., Luna-Barcenas, G., Alvarado, J.F.J., Sánchez, I.C., Macías-Salinas, R., 2005, Simultaneous Correlation of Saturated Viscosities of Pure Gases and Liquids Using the Significant Structure Theory. Ind. Eng. Chem. Res., 44,1960.

Ducoulombier, D., Zhou, H., Boned, C., Peyrelasse, J., Saint-Guirons, H., Xans, P., 1986, Pressure (1-1000 bars) and Temperature (20-100 °C) Dependence of the Viscosity of Liquid Hydrocarbons. J. Phys. Chem., 90, 1692.

Eyring, H., Ree, T., Hirai, N., 1958, Significant Structures in the Liquid State. I. Proc. Nat. Acad. Sci. USA, 44, 683.

Giri, B.R., Blais, P., Marriot, R.A., 2011, In Carbon Dioxide Sequestration and Related Technologies, Wu, Y., Carroll, J.J., Du, Z. Editors, John Wiley & Sons: Salem, MA.

Guo, X.-Q., Sun, C.-Y., Rong, S.-X., Chen, G.-J., Guo T.-M., 2001, Equations of State Analog Correlations for the Viscosity and Thermal Conductivity of Hydrocarbons and Reservoir Fluids. J. Pet. Sci. Eng., 30, 15.

Lemmon, E.W., McLinden, M.O., Huber, M.L., 2005, NIST Reference Fluid Thermodynamic and Transport Properties, REFPROP 7, NIST Standard Reference Database 23, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Macías-Salinas, R., García-Sánchez, F., Hernández Garduza, O., 2003, Viscosity Model for Pure Liquids Based on Eyring Theory and Cubic EoS. AIChE J., 49 799.

Quiñones-Cisneros, S. E., Zéberg-Mikkelsen, C. K., Stenby, E. H., 2000, The Friction Theory (*f-theory*) for Viscosity Modeling. Fluid Phase Equilib., 169, 249.

Quiñones-Cisneros, S. E., Dieters U-K., 2006, Generalization of the Friction Theory for Viscosity Modeling. J. Phys. Chem. B, 110, 12820.

Peng, D.-Y., Robinson, D.B., 1976, A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam., 15, 59.

Soave, G., 1972, Equilibrium Constants from a Modified Redlich-Kwong Equation of State. Chem. Eng. Sci., 27, 1197.

Stephan, K., Lucas, K., 1979, Viscosity of Dense Fluids. Plenum Press: New York and London.

Vogel, E., Kuchenmeister, C., Bich, E., Laesecke, A., 1998, Reference Correlation of the Viscosity of Propane. J. Phys. Chem. Ref. Data, 27, 947.