

Reference Correlation of the Viscosity of *n*-Hexane from the Triple Point to 600 K and up to 100 MPa

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This paper contains new, representative reference equations for the viscosity of *n*-hexane. The equations are based in part upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. The correlations are valid from the triple point to 600 K, and at pressures up to 100 MPa. We estimate the expanded uncertainty at a 95% confidence level to be 2% for the liquid phase at temperatures from the triple point to 450 K and pressures to 100 MPa. For the liquid at 450–600 K at pressures to 100 MPa, the expanded uncertainty at the 95% confidence level is 6%, and is 0.3% for the low-density gas at pressures to 0.3 MPa. © 2013 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [<http://dx.doi.org/10.1063/1.4818980>]

Key words: critical phenomena; *n*-hexane; transport properties; viscosity.

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1. Introduction

In a series of recent papers, new reference correlations for the thermal conductivity of a series of fluids^{1–7} covering a wide range of conditions of temperature and pressure were reported. In this paper, the methodology adopted for thermal conductivity is extended to developing a new reference correlation for the viscosity of *n*-hexane.

The goal of this work is to critically assess the available literature data, and provide a wide-ranging correlation for the viscosity of *n*-hexane that is valid over gas, liquid, and supercritical states, and that incorporates densities provided by a short-form equation of state (EOS) of Span and Wagner.⁸

2. Methodology

The viscosity η can be expressed⁹ as the sum of four independent contributions, as

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

where ρ is the molar density, T is the absolute temperature, and the first term, $\eta_0(T) = \eta(0, T)$, is the contribution to the viscosity in the dilute-gas limit, where only two-body molecular interactions occur. The linear-in-density term, $\eta_1(T)\rho$, known as the initial density dependence term, can be separately established with the development of the Rainwater-Friend theory^{10–12} for the transport properties of moderately dense gases. The critical enhancement term, $\Delta\eta_c(\rho, T)$, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the viscosity at the critical point. Finally, the term $\Delta\eta(\rho, T)$, the residual term, represents the contribution of all other effects to the viscosity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer.

The identification of these four separate contributions to the viscosity and to transport properties in general is useful because it is possible, to some extent, to treat $\eta_0(T)$, $\eta_1(T)$, and $\Delta\eta_c(\rho, T)$ theoretically. In addition, it is possible to derive information about both $\eta_0(T)$ and $\eta_1(T)$ from experiment. In contrast, there is little theoretical guidance concerning the

residual contribution, $\Delta\eta(\rho, T)$, and therefore its evaluation is based entirely on experimentally obtained data.

The analysis described above should be applied to the best available experimental data for the viscosity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data, employed in the development of the correlation, and secondary data, used simply for comparison purposes. According to the recommendation adopted by the Subcommittee on Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry, the primary data are identified by a well-established set of criteria.¹³ These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

3. The Correlation

Table 1 summarizes, to the best of our knowledge, the experimental measurements^{14–20} of the viscosity of *n*-hexane. We have included 107 sets in the table. From these sets, 10 were considered as primary data. Table 1 shows that most of the secondary data sets consist of a few measurements over a limited temperature range near ambient pressure and that many of the secondary data sets fail to provide the sample purity.

The data of Oliveira and Wakeham¹⁴ and Assael *et al.*¹⁵ were obtained in absolute vibrating-wire viscometers with an uncertainty of less than 0.5%, and these sets were considered as primary data. Also in the primary data set, the measurements of Berstad¹⁶ and Knapstad *et al.*,¹⁷ performed in absolute oscillating-cup instruments with 0.5% uncertainty at 0.1 MPa, rising to 1.1% at high pressures, were included. The measurements of *n*-hexane viscosity in the vapor phase of Vogel and Strehlow,¹⁹ obtained in an absolute oscillating-disk viscometer with an uncertainty of 0.15%–0.30%, were also considered as primary data. Capillary viscometers were employed by Bauer and Meerlender²⁰ and Grigor'ev *et al.*,¹⁸ with corresponding uncertainties 0.3% and 0.9%, and these two sets were also included in the primary data. Furthermore, the measurements of Dymond and Young²¹ obtained in a capillary viscometer along the saturation line, with a 1% uncertainty, were also included in the primary data. Finally, after careful consideration, two more sets were included in order to extend the range of the correlation; the high-pressure measurements of Dymond *et al.*²² obtained in a falling-body viscometer with a 2% uncertainty, and the measurements near the critical

TABLE 1. Viscosity measurements of *n*-hexane

1st author	Year of publication	Technique employed ^a	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary data							
Oliveira ¹⁴	1992	VBW-Abs	99.99	0.5	38	303–348	0.1–150 ^b
Assael ¹⁵	1991	VBW-Abs	99.00	0.5	15	298	0.1–71
Berstad ¹⁶	1989	OCup-Abs	99.50	1.1	37	293–437	0.69–45
Knapstad ¹⁷	1989	OCup-Abs	99.00	0.5	7	288–327	0.1
Grigor'ev ¹⁸	1988	Cap	99.29	0.9	53	178–323	0.1–59
Vogel ¹⁹	1988	OD-Abs	99.93	0.15–0.3	82	298–631	0.01–0.31
Bauer ²⁰	1984	Cap	99.00	0.3	2	293–298	0.101
Dymond ²¹	1980	Cap	99.00	1.0	12	283–393	0.01–0.4
Dymond ²²	1980	FB	99.00	2.0	17	298–373	0.1–150 ^b
Agae ²³	1963	Cap	99.80	1–3	291	448–548 ^c	0.101–50 ^c
Secondary data							
Guerrero ²⁴	2011	Cap	99.00	2.0	4	283–313	0.101
Rathnam ²⁵	2010	Cap	99.00	na	3	303–313	0.101
Dominguez ²⁶	2009	Cap	99.50	na	1	298	0.101
Feitosa ²⁷	2009	VBT	98.50	0.4	1	293	0.101
Sastry ²⁸	2009	Cap	na	0.3	2	298–308	0.101
Bandres ²⁹	2008	Cap	99.00	2.0	3	283–313	0.101
Fang ³⁰	2008	Cap	99.90	1.0	3	293–303	0.101
Shukla ³¹	2008	Cap	na	0.6	1	298	0.101
Dubey ³²	2007	Cap	99.00	2.0	1	298	0.10
Reddy ³³	2007	Cap	99.50	0.3	1	303	0.101
Tian ³⁴	2007	Cap	99.40	1.0	8	293–328	0.101
Kumagai ³⁵	2006	FB	98.00	2.9	16	273–333	0.10–30
Baragi ³⁶	2006	VBT	99.00	0.3	3	298–308	0.101
Iloukhani ³⁷	2006	Cap	na	0.7	3	293–303	0.101
Modarress ³⁸	2006	Cap	99.00	0.3	3	298–313	0.101
Rodriguez ³⁹	2006	Cap	99.50	0.3	4	293–313	0.101
Al-Jimaz ⁴⁰	2005	Cap	99.00	1.0	3	293–303	0.10
Tripathi ⁴¹	2005	Cap	99.00	1.0	1	298	0.101
Yang ⁴²	2004	Cap	99.50	1.0	5	293–333	0.101
Bolotnikov ⁴³	2003	Cap	99.70	0.5	9	293–333	0.101
Dominguez ⁴⁴	2003	Cap	99.00	2.0	2	298–313	0.101
Nayak ⁴⁵	2003	Cap	99.00	0.3	3	298–308	0.101
Oswal ⁴⁶	2003	Cap	98.50	1.0	1	303	0.10
Comelli ⁴⁷	2002	Cap	99.50	0.7	1	298	0.101
Garcia ⁴⁸	2002	RB	99.50	na	1	278–318	0.101
Peng ⁴⁹	2002	Cap	99.60	0.8	1	298	0.101
Chowdhury ⁵⁰	2001	Cap	95.00	0.9	3	303–323	0.101
Gascon ⁵¹	2001	Cap	99.00	na	2	298–313	0.101
Postigo ⁵²	2001	Cap	99.50	1.7	3	283–313	0.101
Tu ⁵³	2001	Cap	na	0.8	1	298	0.101
Lal ⁵⁴	2000	Cap	na	na	1	298	0.101
Aralaguppi ⁵⁵	1999	Cap	99.80	0.3	3	298–308	0.101
Barnes ⁵⁶	1999	Cap	na	3.0	1	303	0.101
Casas ⁵⁷	1998	Cap	99.00	0.1	1	298	0.101
Aminabhavi ⁵⁸	1997	Cap	99.60	3.0	3	298–308	0.10
Nath ⁵⁹	1997	na	na	0.7	1	298	0.101
Orge ⁶⁰	1997	FB	99.00	2.0	1	298	0.101
Sastry ⁶¹	1996	Cap	na	1.0	2	303–313	0.101
Aucejo ⁶²	1995	Cap	99.00	0.6	1	298	0.10
Franjo ⁶³	1995	Cap	99.50	0.1	1	298	0.101
Rived ⁶⁴	1995	Cap	99.00	0.1	1	303	0.101
Papaioannou ⁶⁵	1994	FB	99.50	1.0	12	298	0.10–52
De Lorenzi ⁶⁶	1994	Cap	99.00	na	1	298	0.101
Kiran ⁶⁷	1992	FB	99.00	3.0	76	313–448	0.21–65.85
Cooper ⁶⁸	1991	Cap	na	na	1	293	0.101
Abdelraziq ⁶⁹	1990	OQ	na	0.5	7	293–318	0.101
Chevalier ⁷⁰	1990	Cap	na	na	1	298	0.101
Iwahashi ⁷¹	1990	Cap	99.80	na	2	298–323	0.101
Sekar ⁷²	1990	Cap	na	0.5	1	303	0.101
Grachev ⁷³	1989	OCyl	99.93	0.8–8	128	473–623	1–60
Schrodt ⁷⁴	1989	Cap	na	0.2	1	297	0.101
Chandrasekhar ⁷⁵	1988	Cap	na	1.0	1	303	0.101
Rao ⁷⁶	1988	Cap	na	0.5	1	298	0.101

TABLE 1. Viscosity measurements of *n*-hexane—Continued

1st author	Year of publication	Technique employed ^a	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Awwad ⁷⁷	1986	Cap	99.50	na	1	298	0.101
Craubner ⁷⁸	1986	Cap	na	na	1	293	0.101
Singh ⁷⁹	1985	Cap	na	na	1	298	0.101
Singh ⁸⁰	1984	Cap	na	0.1	4	303–333	0.101
Wei ⁸¹	1984	Cap	na	na	1	298	0.101
Sreenivasulu ⁸²	1982	Cap	na	0.5	1	303	0.101
Kashiwagi ⁸³	1982	TCr	99.00	2.0	48	288–327	0.1
Asfour ⁸⁴	1981	Cap	99.00	1.7	1	298	0.101
Teja ⁸⁵	1981	Cap	na	1.0	3	298–323	0.101
Isdale ⁸⁶	1979	FB	99.00	2.0	29	298–373	0.1–500
Gouel ⁸⁷	1978	RB	na	5.0	51	292–393	0.1–40
Medani ⁸⁸	1977	RB	na	na	12	353–463	0.14–1.53
Bulanov ⁸⁹	1975	Cap	na	1.0	60	373–473	0.11–2.53
Diaz Pena ⁹⁰	1975	Cap	99.50	na	9	323–408	0.05–0.55
Moore ⁹¹	1974	Cap	na	na	4	293–313	0.101
Strumpf ⁹²	1974	TCr	99.00	na	8	290–323	0.101
Naziev ⁹³	1972	Cap	na	na	30	297–333	0.101–39
Eicher ⁹⁴	1972	Cap	99.95	0.2	7	266–316	0.101
Heric ⁹⁵	1972	Cap	na	0.0	1	298	0.101
Ghai ⁹⁶	1971	Cap	99.95	na	1	298	0.101
Ratcliff ⁹⁷	1971	Cap	na	na	1	298	0.101
Brazier ⁹⁸	1969	FB	na	na	3	273–333	0.1
Kuss ⁹⁹	1969	Cap	99.60	0.2	6	313	0.1–148
Johari ¹⁰⁰	1968	Cap	na	1.0	1	298	0.101
Diaz Pena ¹⁰¹	1967	Cap	99.50	na	12	313–423	0.03–0.35
Ridgway ¹⁰²	1967	Cap	na	0.3	1	293	0.101
Pariset ¹⁰³	1961	Cap	na	2.0	8	313–454	0.04–1.33
Reed ¹⁰⁴	1959	Cap	na	na	1	298	0.101
Lambert ¹⁰⁵	1955	Cap	na	na	4	323–351	0.05–0.13
Cummings ¹⁰⁶	1952	Cap	na	na	6	300–450	0.101
Craven ¹⁰⁷	1951	OPend	na	1.0	4	308–350	0.002
McCoubrey ¹⁰⁸	1951	Cap	na	na	6	288–462	0.009
Grunberg ¹⁰⁹	1950	Na	na	na	1	293	0.101
Giller ¹¹⁰	1949	Cap	na	0.5	14	174–293	0.101
Geist ¹¹¹	1946	Cap	na	0.1	3	273–313	0.101
Khalilov ¹¹²	1939	Cap	na	na	15	323–463	0.05–1.54
Andrade ¹¹³	1936	OSph	na	na	2	273–295	0.10
Titani ¹¹⁴	1933	Cap	na	na	7	393–579	0.406–2.5
Shepard ¹¹⁵	1931	Cap	na	0.5	1	298	0.101
Timmermans ¹¹⁶	1928	na	na	na	2	288, 303	0.101
Bridgman ¹¹⁷	1926	FB	na	10.0	1	303	0.101
Batschinski ¹¹⁸	1913	Cap	na	na	7	273–333	0.101
Drapier ¹¹⁹	1911	Cap	na	na	5	289–296	0.01–0.02
Thorpe ¹²⁰	1894	Cap	na	na	7	273–333	0.101

^aAbs, Absolute; Cap, Capillary; FB, Falling Body; na, not available; OCup, Oscillating Cup; OCyl, Oscillating Cylinder; OD, Oscillating Disk; OQ, Oscillating Quartz; OPend, Oscillating Pendulum; OSph, Oscillating Sphere; RB, Rolling Ball; TCr, Torsional Crystal; VBT, Vibrating Tube; VBW, Vibrating Wire.

^bData restricted to 150 MPa.

^cData within 0.2 K of the critical temperature and within 0.1 MPa of the critical pressure were excluded.

temperature of Agaev and Golubev²³ obtained in a capillary viscometer with an uncertainty of 1%–3%.

Figures 1 and 2 show the ranges of the primary measurements outlined in Table 1. The phase of the data, as well as the lack of measurements around the critical point, are apparent. Temperatures for all data were converted to the ITS-90 temperature scale.¹²¹ The development of the correlation requires densities; Span and Wagner⁸ in 2003 reviewed the thermodynamic properties of *n*-hexane and developed an accurate, wide-ranging equation of state up to 600 K and

100 MPa, with an uncertainty of 0.2% to 0.5% in density. Dymond *et al.*¹²² measured the density of *n*-hexane from 298 to 373 K and up to 500 MPa, with an uncertainty of better than 0.04% at high pressures. To test the pressure extrapolation behavior of the equation of Span and Wagner⁸ up to 500 MPa, we compared the densities computed from the EOS with the density measurements of Dymond *et al.*,¹²² and found that although the EOS behaves in a physically reasonable manner to 500 MPa and 1000 K, the experimental liquid-phase densities of Dymond *et al.*¹²² differ from those calculated from the

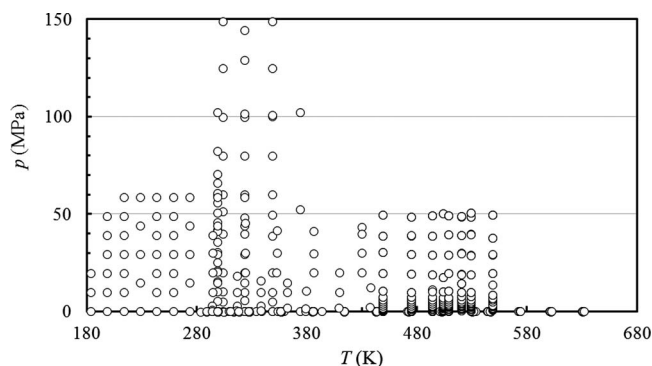


Fig. 1. Temperature-pressure ranges of the primary experimental viscosity data for *n*-hexane.

equation of state by as much as 1% at 500 MPa. This can be acceptable for thermal conductivity correlations,⁵ but for the viscosity it can result in a much larger error. Hence, the equation of Span and Wagner⁸ was employed up to its original limits, that is, 600 K and 100 MPa—limits that also restrict the present viscosity correlation. In addition, deviations for the density in the critical region are much higher. We also adopt the values for the critical point and triple point from their EOS; the critical temperature, T_c , and the critical density, ρ_c , were taken to be equal to 507.82 K and 233.182 kg m⁻³, respectively. The triple-point temperature is 177.83 K, and the molar mass is 86.17536 g mol⁻¹.⁸

3.1. The dilute-gas limit and the initial-density dependence terms

The dilute-gas limit viscosity, $\eta_0(T)$ in $\mu\text{Pa s}$, can be analyzed independently of all other contributions in Eq. (1). According to the kinetic theory, the viscosity of a pure polyatomic gas may be related to an effective collision cross section, which contains all the dynamic and statistical information about the binary collision. For practical purposes, this relation is formally identical to that of monatomic gases and can be written as¹²³

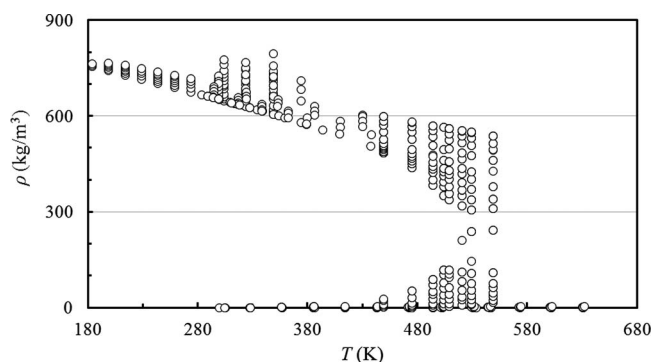


Fig. 2. Temperature-density ranges of the primary experimental viscosity data for *n*-hexane.

$$\eta_0(T) = \frac{0.021357\sqrt{MT}}{\sigma^2 S_\eta^*(T^*)}, \quad (2)$$

where $S_\eta^* = S(2000)/(\pi\sigma^2 f_\eta)$ is a reduced effective cross section, M is the molar mass in g mol⁻¹, σ is the length scaling parameter in nm, and f_η is a dimensionless higher-order correction factor according to Chapman and Cowling.¹²⁴ In the above equation, $S(2000)$ is a generalized cross section that includes all of the information about the dynamics of the binary collisions that govern transport properties, which in turn are governed by the intermolecular potential-energy surface.¹²³ The effective cross section is usually expressed in the functional form

$$\ln S_\eta^*(T^*) = \sum_i \alpha_i (\ln T^*)^i, \quad (3)$$

$$T^* = k_B T / \varepsilon, \quad (4)$$

where T^* is the reduced temperature, ε/k_B is an energy scaling parameter in K, and k_B is Boltzmann's constant.

The temperature dependence of the linear-in-density coefficient of the viscosity, $\eta_1(T)$ in Eq. (1), is very large at subcritical temperatures and must be taken into account to obtain an accurate representation of the behavior of the viscosity in the vapor phase. It changes sign from positive to negative as the temperature decreases. Therefore, the viscosity along an isotherm should first decrease in the vapor phase and subsequently increase with increasing density.¹²³ Vogel *et al.*¹²⁵ have shown that fluids exhibit the same general behavior of the initial density dependence of viscosity, which can also be expressed by means of the second viscosity virial coefficient $B_\eta(T)$ as

$$B_\eta(T) = \frac{\eta_1(T)}{\eta_0(T)}. \quad (5)$$

The second viscosity virial coefficient can be obtained according to the theory of Rainwater and Friend^{10,11} as a function of a reduced second viscosity virial coefficient, $B_\eta^*(T^*)$, as

$$B_\eta^*(T^*) = \frac{B_\eta(T)}{N_A \sigma^3}, \quad (6)$$

where¹²³

$$B_\eta^*(T^*) = \sum_{i=0}^6 b_i (T^*)^{-0.25i} + b_7 (T^*)^{-2.5} + b_8 (T^*)^{-5.5}. \quad (7)$$

In Eq. (6), N_A is Avogadro's constant. The coefficients b_i from Ref. 123 are given in Table 2.

Equations (2)–(7) present a consistent scheme for the correlation of the dilute-gas limit viscosity, $\eta_0(T)$, and the initial density dependence term, $\eta_1(T)$. In the particular case of *n*-hexane, very accurate dilute-gas limit and initial density dependence viscosity values have been presented by Vogel and Strehlow.¹⁹ These values have been used with the regression package ODRPACK (Ref. 126) in order to fit the coefficients

TABLE 2. Coefficients and parameters for Eqs. (3), (7), and (8)

Scaling parameters			
$\varepsilon/k_B = 378.4$ K	$\sigma = 0.6334$ nm		
Coefficients α_i for Eq. (3)			
$\alpha_0 = 0.18760$	$\alpha_1 = -0.48430$	$\alpha_2 = 0.04477$	
Coefficients b_i for Eq. (7) ¹²³			
$b_0 = -19.572881$	$b_1 = 219.73999$	$b_2 = -1015.3226$	
$b_3 = 2471.0125$	$b_4 = -3375.1717$	$b_5 = 2491.6597$	
$b_6 = -787.26086$	$b_7 = 14.085455$	$b_8 = -0.34664158$	
Coefficients c_i for Eq. (8)			
$c_0 = 2.53402335$	$c_1 = -9.724061002$	$c_2 = 0.469437316$	
$c_3 = 158.5571631$	$c_4 = 72.42916856$	$c_5 = 10.60751253$	
$c_6 = 8.628373915$	$c_7 = -6.61346441$	$c_8 = -2.212724566$	

α_i in Eq. (3) and the scaling parameters σ and ε/k_B . The values obtained are shown in Table 2. Figure 3 shows a comparison of the experimental values of B_η from Vogel and Strehlow,¹⁹ along with the values calculated with Eqs. (2)–(7) with the parameters in Table 2. Although Eq. (7) was originally developed for propane, the agreement is quite good. Figure 4 shows a comparison of low-density viscosity data of Vogel and Strehlow¹⁹ with the values calculated with Eqs. (2)–(7). Again, the agreement is good. Based on comparisons with the data of Vogel and Strehlow,¹⁹ we estimate the uncertainty of the correlation for the low-density gas at temperatures from 298 to 631 K to be 0.3%, at a 95% confidence level. Therefore, Eqs. (2)–(7) can be employed for the calculation of the dilute-gas limit viscosity, $\eta_0(T)$ and the initial density dependence term, $\eta_1(T)$.

3.2. The critical enhancement term

Viscosity and thermal conductivity of pure fluids diverge at the critical point due to long-range fluctuations. The critical enhancements can be described by a theoretical crossover model originally developed by Olchowy and Sengers^{127,128} and modified by Luettmer-Strathmann *et al.*¹²⁹ Unlike the

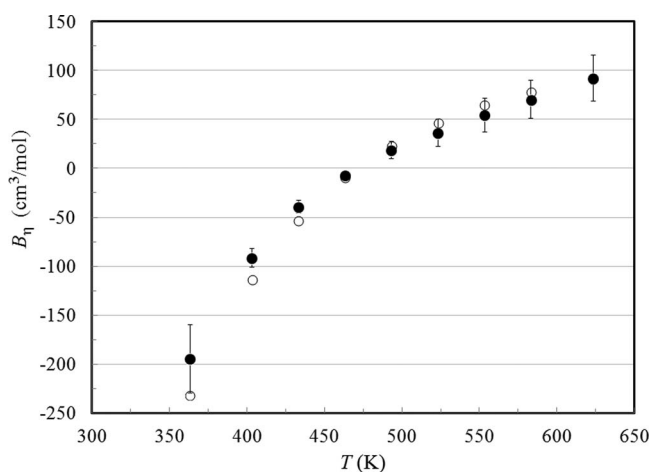


FIG. 3. Comparison of the experimental values of B_η for n -hexane with values calculated from Eqs. (2)–(7) with the parameters in Table 2. Vogel and Strehlow¹⁹ (●), Eqs. (2)–(7) (○).

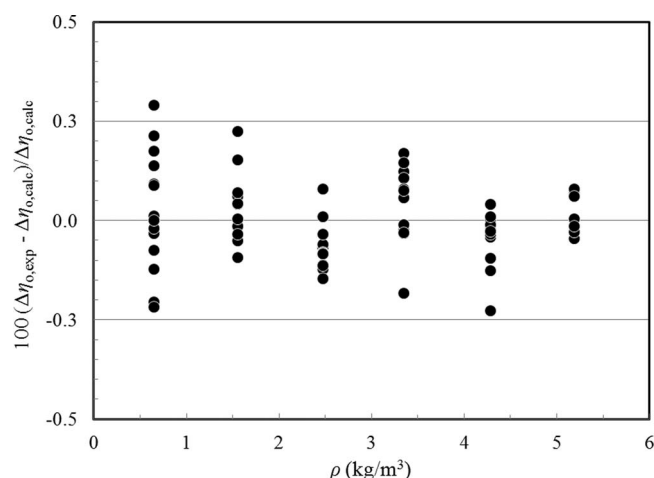


FIG. 4. Percentage deviations of low-density viscosity ($\Delta\eta_0 = \eta_0 + \eta_1(\rho)$) experimental data of n -hexane from the values calculated by Eqs. (2)–(7) as a function of the density. Vogel and Strehlow¹⁹ (●).

critical enhancement in thermal conductivity, the enhancement in viscosity is confined to a small region, becoming relevant only at temperatures and densities very close to the critical point. For some fluids,^{130,131} the ratio $\Delta\eta_c(\rho, T)/\eta(\rho, T)$ exceeds 0.01 only within 1% of the critical temperature of the fluid. There are no reliable data for n -hexane in the critical region. Hence, this contribution is considered negligible and it is not further taken into consideration in this work.

3.3. The residual term

As already stated in Sec. 2, the residual viscosity term, $\Delta\eta(\rho, T)$, represents the contribution of all other effects to the viscosity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer. Because there is little theoretical guidance concerning this term, its evaluation is based entirely on experimentally obtained data.

The procedure adopted during this analysis used symbolic regression software¹³² to fit all the primary data to the residual viscosity. Symbolic regression is a type of genetic programming that allows the exploration of arbitrary functional forms to regress data. The functional form is obtained by use of a set of operators, parameters, and variables as building blocks. Most recently, this method has been used to obtain a correlation for the viscosity of hydrogen.¹³³ In the present work, we restricted the operators to the set (+, −, *, /) and the operands (constant, T_r, ρ_r), with $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$. Various choices of a scaling factor for density were tested, but the best results were obtained using the critical density. In addition, we found the best results when we adopted a form suggested from the hard-sphere model employed by Assael *et al.*,¹³⁴ $\Delta\eta(\rho_r, T_r) = (\rho_r^{2/3} T_r^{1/2}) F(\rho_r, T_r)$, where the symbolic regression method was used to determine the functional form for $F(\rho_r, T_r)$. For this task, the dilute-gas limit and the initial density dependence terms were calculated for each experimental point [employing Eqs. (2)–(7)] and subtracted from the experimental viscosity to obtain the residual term. The

TABLE 3. Evaluation of the *n*-hexane viscosity correlation for the primary data

1st author	Year of publication	AAD (%)	BIAS (%)
Oliveira ¹⁴	1992	0.83	-0.11
Assael ¹⁵	1991	0.80	-0.79
Berstad ¹⁶	1989	1.48	-1.48
Knapstad ¹⁷	1989	0.78	-0.78
Grigor'ev ¹⁸	1988	0.61	-0.23
Vogel ¹⁹	1988	0.10	0.02
Bauer ²⁰	1984	1.48	-1.48
Dymond ²¹	1980	1.05	0.36
Dymond ²²	1980	1.34	-1.18
Agaev ^{23 a}	1963	2.29	0.30
Entire data set		1.56	-0.04

^aExcludes data within 0.2 K of the critical temperature and within 0.1 MPa of the critical pressure.

density values employed were obtained by the equation of state of Span and Wagner.⁸ The final equation obtained was

$$\Delta\eta(\rho, T) = (\rho_r^{2/3} T_r^{1/2}) \left\{ \frac{c_0}{T_r} + \frac{c_1}{c_2 + T_r + c_3 \rho_r^2} + \frac{c_4(1 + \rho_r)}{c_5 + c_6 T_r + c_7 \rho_r + \rho_r^2 + c_8 \rho_r T_r} \right\}. \quad (8)$$

Coefficients c_i are given in Table 2.

Table 3 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as PCTDEV = $100 \cdot (\eta_{\text{exp}} - \eta_{\text{fit}}) / \eta_{\text{fit}}$, where η_{exp} is the experimental value of the viscosity and η_{fit} is the value calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression $\text{AAD} = (\sum |\text{PCTDEV}|) / n$, where the summation is over all n points, the bias percent is found with the expression $\text{BIAS} = (\sum \text{PCTDEV}) / n$. The average absolute percent deviation of the fit is 1.56, and its bias is -0.04%. We estimate the uncertainty at a 95% confidence level to be 2% for the liquid phase at temperatures up to 450 K and pressures to 100 MPa. For the liquid at 450–600 K, the predominant measurements are those of Agaev and Golubev,²³ which are of higher uncertainty and a larger degree of scatter than other primary data, as indicated in Figs. 2–4. In this region, we estimate the expanded uncertainty at the 95% confidence level to be 6%. As mentioned previously, we estimate the expanded uncertainty of the correlation at a 95% confidence level for the low-density gas at temperatures from 298 to 631 K and pressures to 0.3 MPa to be 0.3%.

Figure 5 shows the percentage deviations of all primary viscosity data from the values calculated by Eqs. (1)–(8) as a function of density, while Figs. 6 and 7 show the same deviations but as a function of the temperature and pressure. With the exception of the data set of Agaev and Golubev,²³ all primary data are represented to within 2% over the temperature range 178–437 K at pressures to 100 MPa with the present model. As already discussed above, the data of Agaev and Golubev²³ display larger deviations. Figure 7 shows the extrapolation behavior above 100–200 MPa. We note that, although the present correlation is restricted to 100 MPa because of the validity of the equation of state, it is the authors'

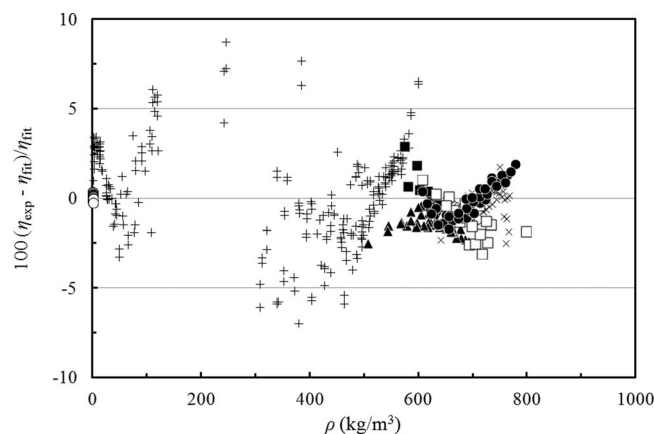


Fig. 5. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the present model as a function of density. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+).

belief that the correlation behaves in a physically reasonable manner at pressures to 500 MPa. However, we estimate that the uncertainties at 500 MPa may be much larger, on the order of 20% to 30%.

In Fig. 6, a previous reference correlation by Dymond and Øye¹³⁵ along the saturation line covering the temperature range from 273 to 355 K is also shown. The Dymond and Øye¹³⁵ correlation has an uncertainty of 1%, and is in agreement with the present correlation within this uncertainty. The correlation of Dymond and Øye¹³⁵ was heavily based on the measurements of Dymond,²¹ and also the measurements of Oliveira and Wakeham¹⁴ and Knapstad *et al.*¹⁷ The present correlation includes measurements of additional investigators; see Table 1.

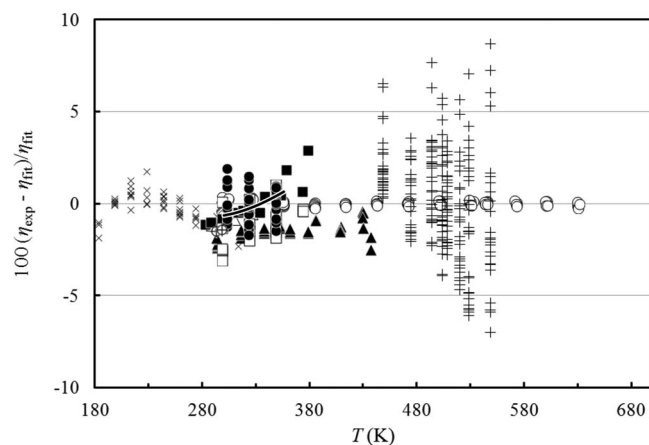


Fig. 6. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the present model as a function of temperature. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+), Dymond and Øye¹³⁵ (–).

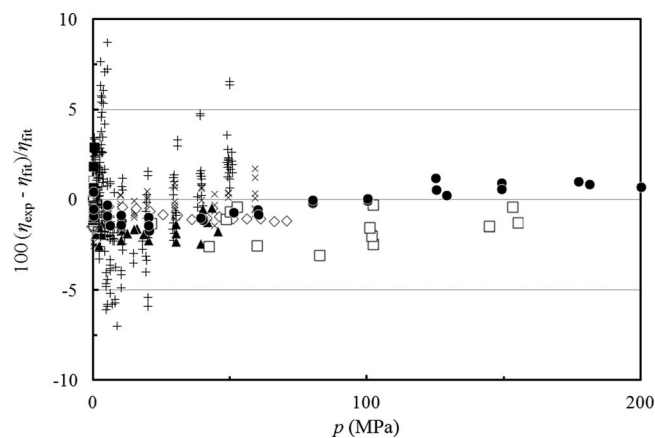


Fig. 7. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the present model as a function of pressure. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+).

Quiñones-Cisneros and Deiters¹³⁶ published a wide-ranging viscosity model based on friction theory applied to several fluids, including *n*-hexane. Figures 8–10 show percentage deviations of the primary data calculated with this friction-theory model as a function of the density the temperature and the pressure, using the same equation of state as was used for the present model (the short Span-Wagner⁸ EOS). The comparisons with the friction theory model indicate that it has similar performance to the present model except for the low-temperature ($T < \sim 270$ K) high-density region. This is not surprising considering that the *n*-hexane friction-theory model presented is very general, did not incorporate the 1988 data set of Grigor'ev *et al.*,¹⁸ and was not developed specifically for *n*-hexane.

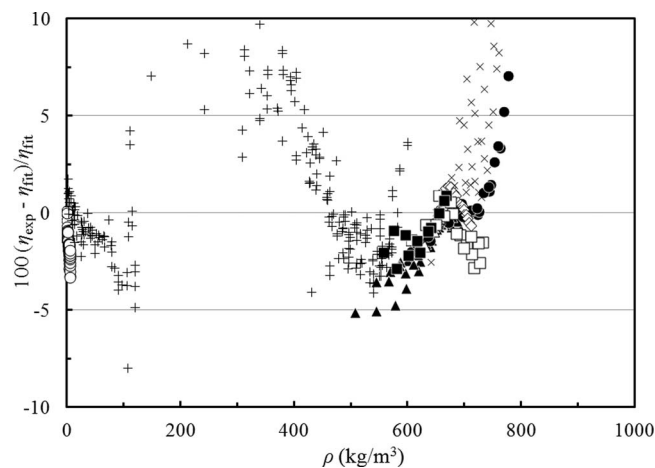


Fig. 8. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the friction-theory model as a function of density. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+).

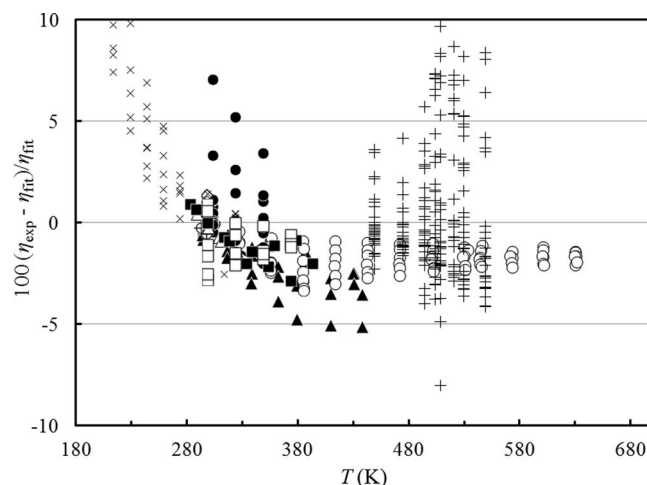


Fig. 9. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the friction-theory model as a function of temperature. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+), Dymond and Øye¹³⁵ (-).

In Table 4, values are given along the saturation line, calculated from the proposed correlation between 250 and 350 K. The uncertainty of these values is 2% at the 95% confidence level. Table 5 shows the AAD and the bias for the secondary data. Finally, Fig. 11 shows a plot of the viscosity of *n*-hexane as a function of the temperature for different pressures.

4. Computer-Program Verification

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

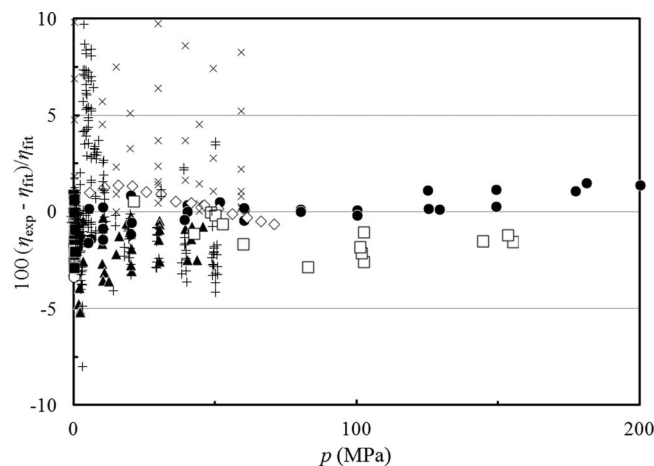


Fig. 10. Percentage deviations of primary experimental data of *n*-hexane from the values calculated by the friction-theory model as a function of pressure. Oliveira and Wakeham¹⁴ (●), Assael *et al.*¹⁵ (◆), Berstad¹⁶ (▲), Knapstad *et al.*¹⁷ (Δ), Grigor'ev *et al.*¹⁸ (×), Vogel and Strehlow¹⁹ (○), Bauer and Meelender²⁰ (◆), Dymond and Young²¹ (■), Dymond *et al.*²² (□), Agaev and Golubev²³ (+).

TABLE 4. Viscosity values of the liquid along the saturation line, calculated by the present scheme

<i>T</i> (K)	ρ (kg m ⁻³)	η (μ Pa s)
250.00	697.89	514.4
260.00	689.05	452.7
270.00	680.16	401.8
280.00	671.19	359.2
290.00	662.14	323.1
300.00	652.98	292.1
310.00	643.70	265.2
320.00	634.26	241.7
330.00	624.66	221.0
340.00	614.86	202.6
350.00	604.84	186.2

TABLE 5. Evaluation of the *n*-hexane viscosity correlation for the secondary data

Ist author	Year of publication	AAD (%)	BIAS (%)
Guerrero ²⁴	2011	2.29	0.50
Rathnam ²⁵	2010	0.84	0.03
Dominguez ²⁶	2009	0.73	0.73
Feitosa ²⁷	2009	4.06	-4.06
Sastry ²⁸	2009	1.72	0.32
Bandres ²⁹	2008	0.83	0.14
Fang ³⁰	2008	3.00	3.00
Shukla ³¹	2008	0.47	-0.47
Dubey ³²	2007	6.05	6.05
Reddy ³³	2007	10.02	10.02
Tian ³⁴	2007	2.19	1.51
Kumagai ³⁵	2006	1.29	-0.55
Baragi ³⁶	2006	4.69	4.69
Ilokhani ³⁷	2006	1.64	-1.20
Modarress ³⁸	2006	1.23	1.23
Rodriguez ³⁹	2006	0.63	0.55
Al-Jimaz ⁴⁰	2005	0.70	0.70
Tripathi ⁴¹	2005	0.40	-0.40
Yang ⁴²	2004	1.35	-1.22
Bolotnikov ⁴³	2003	5.23	5.23
Dominguez ⁴⁴	2003	0.41	-0.41
Nayak ⁴⁵	2003	6.69	6.69
Oswal ⁴⁶	2003	0.91	-0.91
Comelli ⁴⁷	2002	0.05	-0.05
Garcia ⁴⁸	2002	12.59	12.59
Peng ⁴⁹	2002	0.63	0.63
Chowdhury ⁵⁰	2001	3.12	3.12
Gascon ⁵¹	2001	0.02	0.01
Postigo ⁵²	2001	1.93	1.22
Tu ⁵³	2001	2.31	2.31
Lal ⁵⁴	2000	0.39	-0.39
Aralaguppi ⁵⁵	1999	2.31	2.31
Barnes ⁵⁶	1999	7.43	-7.43
Casas ⁵⁷	1998	1.41	-1.41
Aminabhavi ⁵⁸	1997	1.49	1.49
Nath ⁵⁹	1997	0.74	-0.74
Orge ⁶⁰	1997	6.72	6.72
Sastry ⁶¹	1996	1.20	1.20

TABLE 5. Evaluation of the *n*-hexane viscosity correlation for the secondary data—Continued

Ist author	Year of publication	AAD (%)	BIAS (%)
Aucejo ⁶²	1995	1.20	1.20
Franjo ⁶³	1995	3.07	-3.07
Rived ⁶⁴	1995	1.33	-1.33
Papaioannou ⁶⁵	1994	4.00	-3.93
De Lorenzi ⁶⁶	1994	0.37	0.37
Kiran ⁶⁷	1992	2.89	2.64
Cooper ⁶⁸	1991	0.00	0.00
Abdelraziq ⁶⁹	1990	65.89	65.89
Chevalier ⁷⁰	1990	1.40	-1.40
Iwahashi ⁷¹	1990	6.26	6.26
Sekar ⁷²	1990	13.94	13.94
Grachev ⁷³	1989	4.51	-3.03
Schrodt ⁷⁴	1989	2.86	2.86
Chandrasekhar ⁷⁵	1988	0.80	-0.80
Rao ⁷⁶	1988	10.79	10.79
Awwad ⁷⁷	1986	4.89	4.89
Craubner ⁷⁸	1986	0.16	-0.16
Singh ⁷⁹	1985	0.13	-0.13
Singh ⁸⁰	1984	8.34	8.34
Wei ⁸¹	1984	2.04	-2.04
Kashiwagi ⁸³	1982	0.74	-0.64
Sreenivasulu ⁸²	1982	1.03	-1.03
Asfour ⁸⁴	1981	0.33	-0.33
Teja ⁸⁵	1981	0.74	-0.13
Isdale ⁸⁶	1979	10.06	-9.12
Gouel ⁸⁷	1978	3.76	-1.14
Medani ⁸⁸	1977	4.89	-0.97
Bulanov ⁸⁹	1975	2.83	2.55
Diaz Pena ⁹⁰	1975	5.47	5.47
Moore ⁹¹	1974	0.49	0.41
Strumpf ⁹²	1974	2.05	2.05
Naziev ⁹³	1972	2.70	-0.93
Eicher ⁹⁴	1972	0.47	0.38
Heric ⁹⁵	1972	0.13	0.13
Ghai ⁹⁶	1971	0.17	0.17
Ratcliff ⁹⁷	1971	0.24	0.24
Brazier ⁹⁸	1969	2.51	1.72
Kuss ⁹⁹	1969	1.31	-1.20
Johari ¹⁰⁰	1968	1.13	-1.13
Diaz Pena ¹⁰¹	1967	2.31	-0.57
Ridgway ¹⁰²	1967	3.14	-3.14
Parisot ¹⁰³	1961	1.84	1.84
Reed ¹⁰⁴	1959	0.86	-0.86
Lambert ¹⁰⁵	1955	5.63	5.63
Cummings ¹⁰⁶	1952	2.90	-1.90
Craven ¹⁰⁷	1951	8.12	8.12
McCoubrey ¹⁰⁸	1951	1.01	1.01
Grunberg ¹⁰⁹	1950	4.91	4.91
Giller ¹¹⁰	1949	3.55	-3.55
Geist ¹¹¹	1946	0.73	-0.73
Khalilov ¹¹²	1939	11.80	-2.10
Andrade ¹¹³	1936	2.91	2.91
Titani ¹¹⁴	1933	13.70	-12.07
Shepard ¹¹⁵	1931	0.50	-0.50
Timmermans ¹¹⁶	1928	0.45	0.22
Bridgman ¹¹⁷	1926	5.39	5.39
Batschinski ¹¹⁸	1913	3.28	3.28
Drapier ¹¹⁹	1911	2.30	2.30
Thorpe ¹²⁰	1894	3.30	3.30

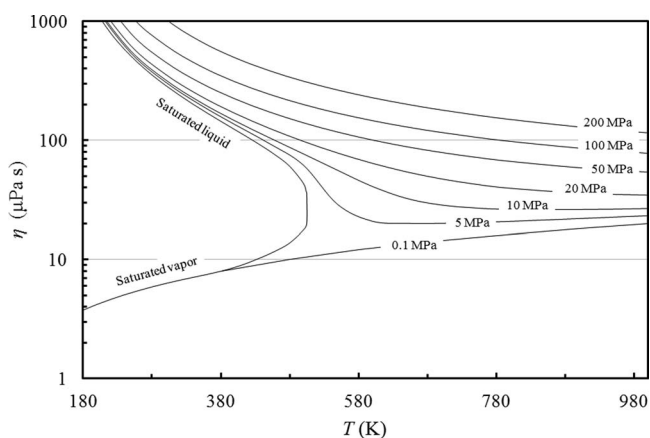


FIG. 11. Viscosity of *n*-hexane as a function of temperature for selected pressures.

TABLE 6. Sample points for computer verification of the correlating equations

T (K)	ρ (kg m^{-3})	η ($\mu\text{Pa s}$)
250.00	0.00	5.2584
400.00	0.00	8.4149
550.00	0.00	11.442
250.00	700.00	528.20
400.00	600.00	177.62
550.00	500.00	95.002

5. Conclusion

A new wide-ranging correlation for the viscosity of *n*-hexane was developed based on critically evaluated experimental data. The correlation is valid from the triple point to 600 K, and at pressures up to 100 MPa. The correlation is expressed in terms of temperature and density, with the density calculated from the equation of state of Span and Wagner.⁸ The average absolute percent deviation of the fit is 1.56%, with bias -0.04% . We estimate the expanded uncertainty at a 95% confidence level to be 2% for the liquid phase at temperatures up to 450 K and pressures to 100 MPa. For the liquid at 450–600 K at pressures to 100 MPa, the expanded uncertainty at the 95% confidence level is 6%, and is 0.3% for the low-density gas at temperatures from 298 to 631 K and pressures to 0.3 MPa.

Acknowledgments

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