

Reference Correlation for the Viscosity of 1,1,1,2-tetrafluoroethane (R-134a) from the Triple Point to 438 K and up to 70 MPa

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We present a new wide-ranging correlation for the viscosity of 1,1,1,2-tetrafluoroethane (R-134a) based on critically evaluated experimental data. The correlation is designed to be used with densities from an existing equation of state, which is valid from the triple point to 438 K, at pressures up to 70 MPa. The estimated uncertainty (at the 95% confidence level) for the viscosity varies depending on the temperature and pressure, from a low of 0.2 % in the dilute-gas range near room temperature, to 2 % along the saturated vapor boundary, 2.5 % for the saturated liquid, and 4 % for some high-pressure regions. The correlation behaves in a physically reasonable manner when extrapolated to pressures above 70 MPa. Comparisons with experimental data at pressures to 400 MPa are given. However, care should be taken when using the correlation outside of the validated range of the equation of state.

Key words: transport properties; viscosity; 1,1,1,2-tetrafluoroethane; R134a; HFC-134a.

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1 Introduction

1,1,1,2-tetrafluoroethane (IUPAC name), commonly known as R-134a or HFC-134a, is a widely-used refrigerant of the hydrofluorocarbon family, first developed to replace its ozone-depleting predecessor, dichlorodifluoromethane (R-12). Its low ozone depletion potential and other beneficial characteristics very early established it as an important alternative refrigerant. Unfortunately, it has a large global warming potential, 1300 [1], and efforts are underway to find replacements [2]. However, it may still be useful as a constituent in refrigerant mixtures [2] and it is often used as a reference fluid for corresponding-states models for refrigerants [3]. For these reasons, there still is interest in correlations for the thermophysical properties of this fluid.

The first correlations for the viscosity of 1,1,1,2-tetrafluoroethane were developed by Huber and Ely [4] in 1992, based on the measurements of Diller et al. [5], Nabizadeh and Mayinger [6], Ruvinski et al. [7], Kumagai and Takahashi [8], and Shankland et al. [9]. The correlation was valid in the temperature range (175 to 424) K and up to 34 MPa, with an uncertainty of about 4%.

In 1993, Krauss et al. [10] also published a viscosity correlation for 1,1,1,2-tetrafluoroethane for the temperature range (290 to 430) K and up to about 30 MPa, also with an uncertainty of about 4%. The correlation of Krauss was also based on the measurements of Nabizadeh and Mayinger [6], Ruvinski et al. [7], as well as the newer measurements of Dowdell and Mathews [11], Oliveira and Wakeham [12], Okubo et al. [13], and Takahashi et al [14].

However, significant discrepancies among early experimental data, as well as large gaps in the temperature-pressure ranges of the available measurements, limited the reliability and validity ranges of the aforementioned viscosity correlations. Hence, a round-robin project was coordinated by the Subcommittee on Transport Properties (now known as The International Association for Transport Properties) of Commission I.2 of the International Union of Pure and Applied Chemistry (IUPAC), to address the issue of erroneous data, mainly in terms of sample impurity and inexperience in measuring the properties of materials that are highly polar [15]. ICI Chemicals and Polymers Ltd., upon request, prepared a certified specially pure sample and supplied, from this sample, nine laboratories to measure its properties. The people involved in this project were M. J. Assael (Aristotle University, Greece), A. Leipertz (Friedrich-Alexander University, Germany), E. MacPherson (National Research Council, Canada), Y. Nagasaka (Keio University, Japan), C. Nieto de Castro (University of Lisbon, Portugal), R. A. Perkins (NIST, USA), K. Ström (Chalmers University of Technology, Sweden), E. Vogel (University of Rostock, Germany) and W. A. Wakeham (Imperial College, U.K.). In this way, the main problem of sample impurities or contamination was controlled. The project was completed in 2000 [16]. The measurements were compared with the baseline correlation of Krauss et al. [10], thus revalidating its uncertainty levels. It is interesting to note that the viscosity of the round-robin sample was measured with an oscillating-disk viscometer, three vibrating-wire viscometers, a falling-ball viscometer, a capillary flow viscometer, and a falling-body viscometer. The largest discrepancy between the round-

robin participants for vapor viscosity was 2.5% with oscillating-disk and vibrating-wire viscometers in the low-density vapor. The largest discrepancy for liquid viscosity was 6% obtained with a falling-ball viscometer at high temperatures, with the maximum deviations between the falling-body and the vibrating-wire viscometers less than 3%. [16].

In 1997, an improved viscosity correlation was presented by Klein et al. [17], stating that it was developed by A. Laesecke (one of his coauthors), and never published. This correlation was valid in the temperature range (200 to 440) K and up to a maximum density of 1550 kg/m^3 , with an average deviation between the correlation and experimental data of 1.69% and a maximum deviation of 5.5%.

Following the publication of the measurements from the round-robin project and new information available, Huber et al. [3] performed a critical evaluation of experimental measurements in 2003 and developed a viscosity reference correlation for 1,1,1,2-tetrafluoroethane, to be used in a corresponding-states prediction of the viscosity of refrigerants with similar chemical nature. Huber et al. [3], employed for the development of the correlation the measurements of Wilhelm and Vogel [18], Shibasaki-Kitakawa et al. [19], Dunlop [20], Pasekov and Ustyuzhanin [21], Dowdell and Mathews [11], and Okubo et al. [13]. The correlation has an estimated uncertainty of 3 % in the temperature range of (213 to 438) K and pressures up to 40 MPa, rising to 8 % in the temperature range (200 to 170) K and at pressures over 40 MPa. It is currently incorporated in REFPROP [22] as the default model for the viscosity of R134a. Note that this correlation exhibits un-physical behavior, such as negative viscosity, upon extrapolation to high pressures outside of its recommended application range. For example, at 200 K this correlation gives negative viscosities above approximately 130 MPa, and at 300 K this behavior occurs at pressures above approximately 315 MPa.

It should finally be mentioned that, in 2006, Scalabrin et al. [23] developed a heuristic, entirely empirical technique for a “multiparameter equation” for the viscosity of 1,1,1,2-tetrafluoroethane, based on the at-the-time current experimental measurements. This correlation covers a slightly wider range of temperatures up to 450 K and pressures no greater than 55 MPa, which is the upper limit of the available data. The Scalabrin et al. [23] equation shows a comparable uncertainty with the Huber et al. [3] correlation, and a slightly better performance in the liquid region.

Since the development of the Scalabrin et al. [23] equation, new measurements of the viscosity of 1,1,1,2-tetrafluoroethane at significantly higher pressures, up to 400 MPa have been published by Laesecke and Bair [24], and low-uncertainty recommended values for the dilute-gas and initial density dependence viscosity, based on a re-evaluation of the Wilhelm and Vogel measurements [18], have also very recently been reported [25]. Hence, there is currently a need for an up-to-date, wide-ranging reference correlation for the viscosity of 1,1,1,2-tetrafluoroethane.

In a series of recent papers, reference correlations for the viscosity of selected common fluids [26-36] have been developed that cover a wide range of temperature and pressure conditions, including the gas, liquid, and supercritical phases. In this paper, the methodology adopted in the aforementioned papers is extended to developing a new reference correlation for the viscosity of 1,1,1,2-

tetrafluoroethane. The analysis that will be described is based on 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 [37]. 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 higher uncertainty, provided they are consistent with other lower uncertainty data or with theory. In all cases, the uncertainty claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

2 The Correlation

The viscosity η can be expressed [26, 29-32] 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 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 [38-40] 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. This term for viscosity is significant only in the region very near the critical point, as shown in Vesovic et al. [41] and Hendl et al. [42]. Since data close to the critical point are unavailable, $\Delta\eta_c(\rho, T)$ will be set to zero in Eq. 1 and not discussed further in this work. 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 an empirical equation obtained by fitting experimental data.

Table 1 summarizes, to the best of our knowledge, all the available experimental measurements of the viscosity of 1,1,1,2-tetrafluoroethane reported in the literature. In the same table, the technique employed, the purity, the uncertainty as reported by the original authors, the number of measurements, as well as the range of temperatures and pressures investigated are also shown.

Table 1 Viscosity measurements of 1,1,1,2-tetrafluoroethane

Investigators/reference	Publ. Year	Technique employed ^a	Purity ^b (%)	Uncertainty (%)	No. of data ^c	Temperature range (K)	Pressure range (MPa)
<i>Primary data</i>							
Vogel and Bich [25] ^d	2021	OD	99.9	0.2-0.3*	71	297-439	0.03-0.3
Alam et al. [43]	2018	Cap	99.50	3.0*	19	313-356	1.7-4.2
Meng et al. [44]	2013	VW	99.9	2.0*	54	253-353	1-30
Laesecke and Bair [24]	2011	FCyl	Lab	3.5	59	293-438	10-400
Kumagai and Yokoyama [45]	2000	Cap	99.8	0.5	8	273-343	0.3-2.1
Oliveira and Wakeham [46] ^{RR}	1999	VW	99.9	2	14	243-343	0.08-2.1
Shibasaki-Kitakawa et al. [19] ^H	1998	OD	99.9	0.3	126	298-423	0.1-5.6
Assael and Polimatidou [47] ^{RR}	1997	VW	99.9	1	22	273-333	0.1-1.5
Pàdua et al. [48] ^{RR}	1996	VW	99.9 ^{RR}	2.5	37	248-298	0.1-100
Heide [49]	1996	FBod	99.9	2	14	223-353	0.02-2.6
Dunlop [20] ^H	1994	Cap	99.2	0.3	1	298	0.1
Pasekov and Ustyuzhanin [21] ^H	1994	Cap	99.83	0.9-1.3	37	275-371	0.27-0.6
Assael et al. [50] ^{RR}	1994	VW	99.91	1	32	273-333	0.9-15
Dowdell and Matthews [11] ^H	1993	Cap	99.95	0.4	6	308-403	0.1
Oliveira and Wakeham [12] ^{RR}	1993	VW	99.9	0.6	60	238-343	0.1-51
Okubo et al. [13] ^H	1992	Cap	99.9	1.3	81	213-324	1.6-30.2
Ruvinskij et al. [7]	1990	Cap	99.67	1.2-1.5	34	257-404	0.3-6.4
<i>Secondary data</i>							
Miyara et al. [43]	2018	Cap	99.5	3.1	19	313-356	1.7-4.2
Zhao et al. [51]	2014	SLS	99.9	2-6*	8	302-368	0.76-3.2
Meng et al. [44]	2011	VW	99.9	2.8*	43	258-338	1-40
Comuñas et al. [52]	2003	FBod	99.94	2-4	70	293-373	10-140
Fröba et al. [53]	2000	SLS	99.98	2-4	13	243-363	0.08-3.2
Laesecke et al. [54]	1999	Cap	Lab	2-2.2	91	241-350	0.1-2.5
Pàdua et al. [48]	1996	VW	99.9	2	5	198-298	0.01-0.66
Han et al. [55]	1995	Cap	99.95	1	21	233-333	0.05-1.7
Geller et al. [56]	1994	Cap	na	1.2	Eqn	253-373	0.29-4
Burke et al. [57]	1994	FBal	na	na	7	233-353	0.1-2.6
Diller et al. [5]	1993	TC	Lab	2	93	175-320	0.001-33.7
Bivens et al. [58]	1993	Cap	na	1.2	8	253-370	0.13-3.7
Ripple and Matar [59]	1993	Cap	99.98	3-5	14	250-306	0.12-0.8
Belyaeva et al. [60]	1993	FBod	99.91	2.8	79	293-360	0.7-16.3
Nabizadeh and Mayinger [6]	1992	OD	na	0.5	41	302-424	0.1-6.4
Lavrachenko et al. [61]	1992	Cap	99.67	1.5	23	258-361	0.3-6.4

Heide and Lippold [62]	1990	RBal	na	na	Eqn	233-353	0.1-2.6
Shankland et al. [9]	1988	Cap	99.9	na	12	251-343	0.1-2.1

^H Measurements employed in the development of the 2003 reference correlation of Huber et al. [3]

^{RR} Measurements performed for the Round-Robin sample [15]

^a Cap, Capillary; FBal, Falling Ball; FBod, Falling Body; FCyl, Falling Cylinder; OD, Oscillating Disc; RBal, Rolling Ball; SLS, Surface Light Scattering; TC, Torsional Crystal; VW, Vibrating Wire.

^b Lab, further purified in the Laboratory; na, not available.

^c Eqn, Equation.

^d Replaces Wilhelm and Vogel [18]

^e Replaces Kumagai and Takahashi [8]

* Uncertainty quoted at the 95% confidence level.

Since the reference correlation developed in 2003 by Huber et al. [3] was based on critically evaluated data, those data (Shibasaki-Kitakawa et al. [19], Dunlop [20], Pasekov and Ustyuzhanin [21], Dowdell and Mathews [11], Okubo et al. [13], and Wilhelm and Vogel [18]), marked by superscript “H” on Table 1, were kept as primary data. We also note that Vogel and Bich [25] recently published re-evaluated experimental viscosity measurements originally published by Wilhelm and Vogel [18] in 1996. Hence, we only included the latest set from Vogel and Bich [25]. Moreover, we included in the primary set the measurements performed under the aforementioned round-robin project, as those measurements were performed in the exact same sample of R134a, with the utmost care. Those measurements (Oliveira and Wakeham [46], Assael and Polimatidou [47], Pàdua et al. [48], Assael et al. [50], and Oliveira and Wakeham [12]) are marked with a superscript “RR” in Table 1.

Since the 2003 Huber et al. [3] correlation, new high-pressure measurements have been published. The measurements of Laesecke and Bair [24], performed with a falling-cylinder viscometer and 3.5% uncertainty, extend to 400 MPa, while the measurements of Meng et al. [44] performed with a vibrating-wire instrument and a 2 % uncertainty, up to 30 MPa. Both these sets were included in the primary data set. We also included the 2018 measurements of Alam et al. [43] performed in a capillary viscometer with a 3% uncertainty (at the 95% confidence limit).

Finally, three additional sets were included in the primary data set: the very-low uncertainty (0.5%) measurements of Kumagai and Yokoyama [45], and the falling-body measurements of Heide [49] and the capillary measurements of Ruvinskij et al. [7] as they extend to low temperatures and have a low uncertainty of 2% and 1.5% respectively.

We did not include in the primary data set

- The measurements of Comuñas et al. [52], as the middle range pressure measurements (about 30 MPa) seem to be about 10% higher than all the rest [24].
- The 1999 measurements of Laesecke et al. [54] as they were performed with a sealed gravitational capillary viscometer with straight vertical capillary, for which doubts have been expressed about its proper operation [63].

- The 1995 measurements of Han et al. [55] as they were not corrected for the buoyancy of the vapor [54].
- The 1988 measurements of Shankland et al. [9], as did not report the diameter of the capillary coil, the number of coils of the instrument, while the measurements were not corrected for the buoyancy of the vapor or for the radial acceleration of the fluid flow in the coil [54].
- Measurements performed with an uncertainty of over 3% (Zhao et al. [51], Fröba et al. [53], Ripple and Matar [59]), lacking a quoted uncertainty (Burke et al. [57], Heide and Lippold [62], Shankland et al. [9]), without a stated purity (Geller et al. [56], Bivens et al. [58], Heide and Lippold [62]) or that were identified as having large errors (Diller et al. [5]) in earlier studies [23].

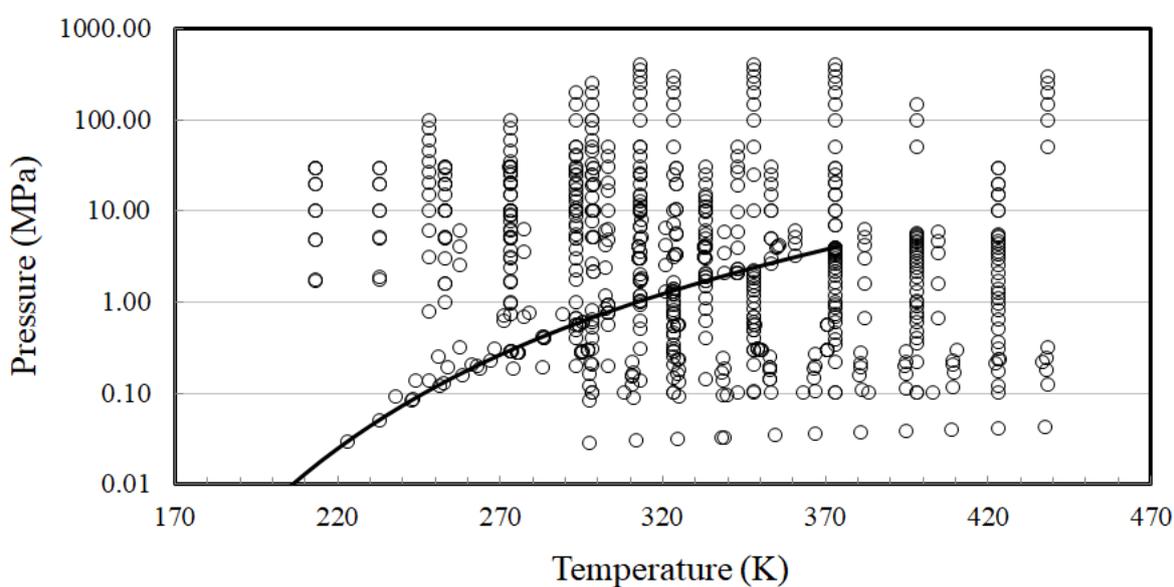


FIG. 1 Temperature-pressure ranges of the primary experimental viscosity data for 1,1,1,2-tetrafluoroethane. Solid curve denotes the saturation boundary.

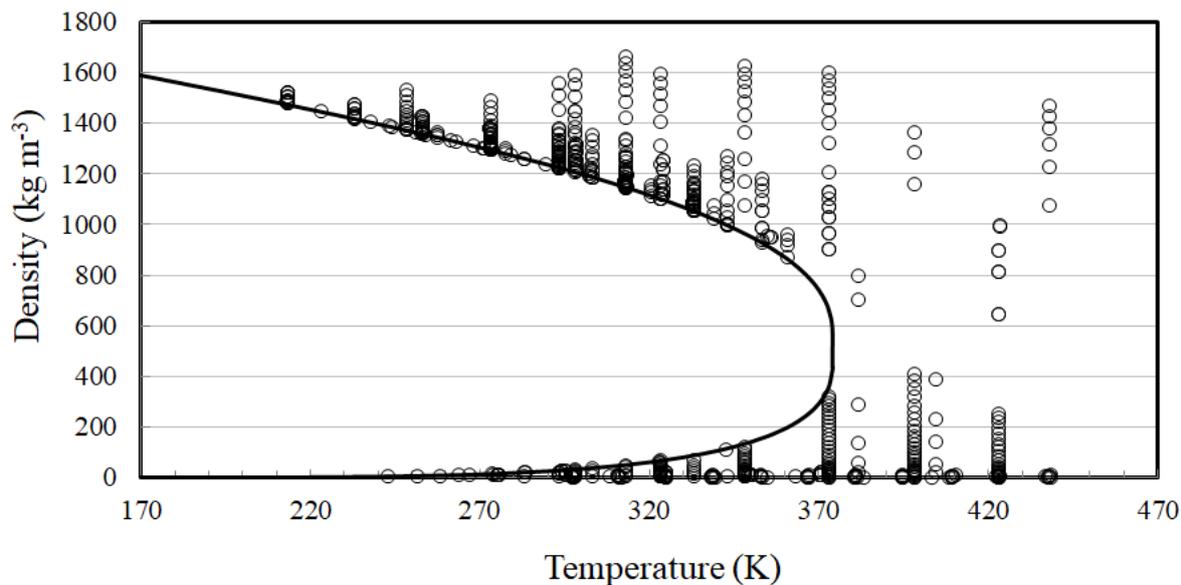


FIG. 2 Temperature-density ranges of the primary experimental viscosity data for 1,1,1,2-tetrafluoroethane. Solid curve denotes the saturation boundary.

Figures 1 and 2 show the ranges of the primary measurements outlined in Table 1, and the phase boundary. The development of the correlation requires densities. In 1994, Tillner-Roth and Baehr [64] developed an accurate, wide-ranging equation of state (EOS) that is valid from the triple point up to 455 K and 70 MPa, while in 2004 Astina and Sato proposed a new equation of state valid over the same ranges. We adopt the Tillner-Roth and Baehr [64] equation of state because: 1) it is recommended [65] by Annex 18 of the International Energy Agency (IEA), and 2) has an uncertainty in density of 0.05%, while the Astina and Sato equation [66] reports 0.1%. The Tillner-Roth and Baehr [64] equation of state is also the one recommended in REFPROP [22]. As indicated in Fig. 1, some of the primary data exceed 70 MPa, and we use the equation of state in an extrapolation mode. For consistency we adopt the values for the critical point from Tillner-Roth and Baehr [64], namely the critical temperature, T_c , and the critical density, ρ_c , are 374.21 K and 511.9 kg m⁻³, respectively. For the triple-point temperature we use the value given by Magee [64, 67], 169.85 K, that also was adopted by Tillner-Roth and Baehr [64].

2.1 The dilute-gas limit viscosity term

The dilute-gas limit viscosity, $\eta_0(T)$ in $\mu\text{Pa s}$, can be analyzed independently of all other contributions in Eq. 1. As already discussed in the previous section, in their very recent work, Vogel and Bich [25] re-evaluated the experimental values originally proposed by Wilhelm and Vogel [18] in 1996 for the viscosity of 1,1,1,2-tetrafluoroethane, as improved values are now available for the viscosity of the calibration fluids, argon and nitrogen. The re-evaluated values were subsequently employed to develop a correlation for the viscosity of 1,1,1,2-tetrafluoroethane in the dilute-gas range. This new dilute-gas

viscosity correlation for 1,1,1,2-tetrafluoroethane covers the temperature range from (297 to 438) K with an uncertainty of up to 0.3 %, and it can be extrapolated safely to temperatures as low as 1 K and as high as 1500 K. Therefore, the correlation of Vogel and Bich [25] will form the dilute-gas viscosity contribution of 1,1,1,2-tetrafluoroethane in this work and it is described by the following equation:

$$\eta_0(T) = \frac{T^{1/2}}{G_\eta(T)}, \quad (2)$$

where $\eta_0(T)$ is in $\mu\text{Pa}\cdot\text{s}$, T is the temperature in K, and $G_\eta(T)$ is given by:

$$G_\eta(T) = f_1 T \exp(-2T^{1/3}) + \frac{f_2 + f_3 \exp(-T^{1/3})}{T^{1/3}} + f_4 \exp(-\frac{1}{T^{1/3}}). \quad (3)$$

The coefficients f_1, f_2, f_3 , and f_4 for 1,1,1,2-tetrafluoroethane are given in Table 2, while Figure 3 shows the dilute-gas limit viscosity η_0 as a function of the temperature, calculated by the scheme of Eqs. 2 and 3 and the re-evaluated zero-density values of Vogel and Bich [25].

Table 2 Coefficients f_i of Eq. 3

i	f_i
1	-17.2940
2	11.15987
3	292.165
4	-0.296506

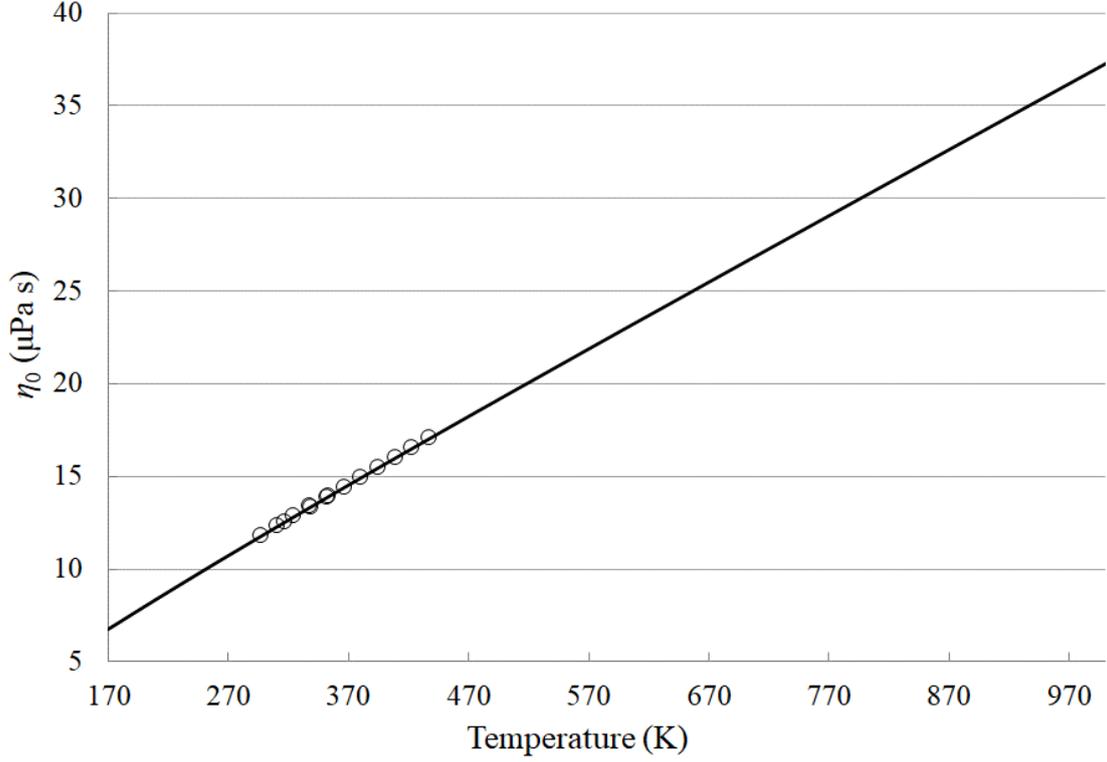


FIG. 3 Dilute-gas limit viscosity η_0 as a function of the temperature, calculated by the scheme of Eqs. 2 and 3. Vogel and Bich [25] (\circ).

2.2 The initial-density dependence viscosity term

Following previous recent work [34-36] we use the approach of Vogel et al. [68] that has demonstrated that fluids exhibit the same general behavior of the initial density dependence of viscosity, expressed by means of the second viscosity virial coefficient $B_\eta(T)$ in $\text{m}^3 \text{kg}^{-1}$, as

$$B_\eta(T) = \frac{\eta_1(T)}{\eta_0(T)}. \quad (4)$$

In the above equation, if the dilute-gas limit viscosity, $\eta_0(T)$, is expressed in $\mu\text{Pa s}$, then the initial-density viscosity, $\eta_1(T)$, will be expressed in $\mu\text{Pa s m}^3 \text{kg}^{-1}$. The second viscosity virial coefficient is obtained using the theory of Rainwater and Friend [38, 39] as a function of a reduced second viscosity virial coefficient, $B_\eta^*(T^*)$,

$$B_\eta^*(T^*) = \frac{B_\eta(T) M}{N_A \sigma^3}, \quad (5)$$

where [39]

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

In Eq. 5, M is the molar mass in g mol^{-1} given in Table 3, T^* is the scaled temperature $= T/(\varepsilon/k_B)$, and N_A is the Avogadro constant. The general coefficients b_i from Ref. [69] are given in Table 3, together with the scaling parameters σ and ε/k_B (specific for R134a) proposed by Vogel and Bich [25].

Table 3 Coefficients and parameters for Eqs. 5 and 6

Molar mass		
102.032 g mol^{-1}		
Scaling parameters [18]		
$\varepsilon/k_B = 277.99 \text{ K}$	$\sigma = 0.48 \text{ 499 nm}$	
Coefficients b_i for Eq. 6 [69]		
$b_0 = -19.572 \text{ 881}$	$b_1 = 219.739 \text{ 99}$	$b_2 = -1015.322 \text{ 6}$
$b_3 = 2471.012 \text{ 5}$	$b_4 = -3375.171 \text{ 7}$	$b_5 = 2491.659 \text{ 7}$
$b_6 = -787.260 \text{ 86}$	$b_7 = 14.085 \text{ 455}$	$b_8 = -0.346 \text{ 641 58}$

Figure 4 shows the calculated values of the initial-density viscosity coefficient, employing the scheme described by Eqs. 2-6.

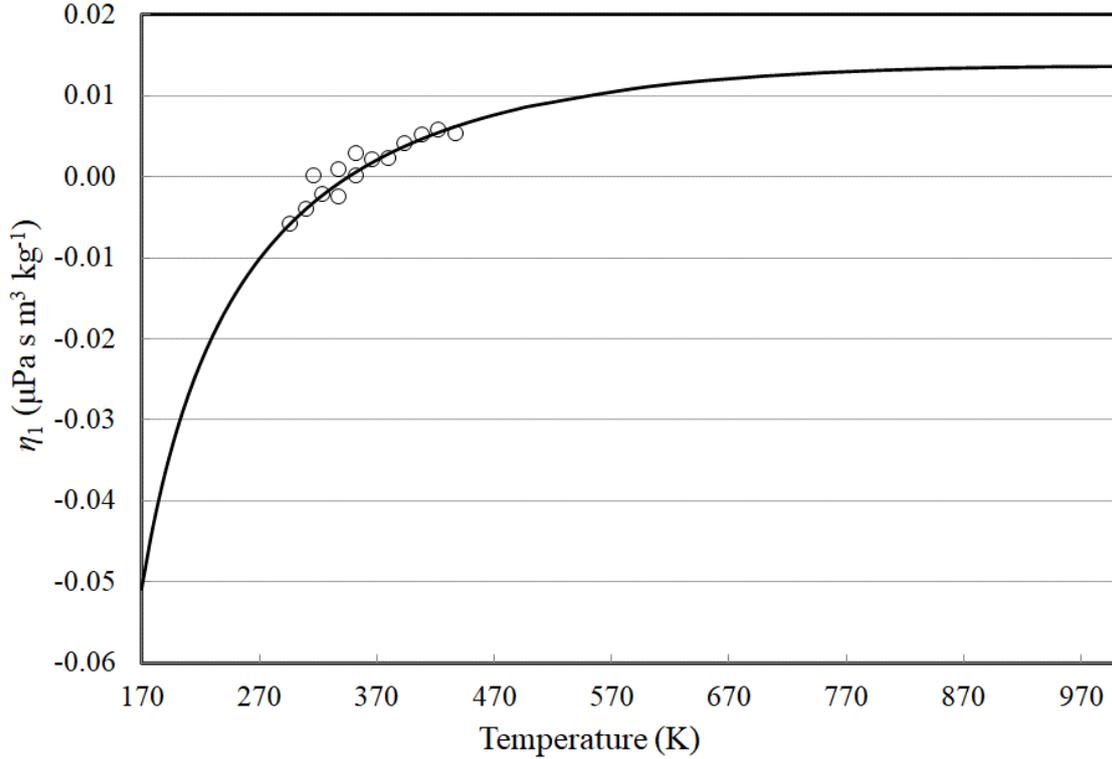


FIG. 4 Initial-density viscosity coefficient η_1 as a function of the temperature, calculated from the scheme of Eqs. 2-6. Vogel and Bich [25] (○).

2.3 The residual term

Following recent similar work[34-36], we use symbolic regression software [70] to fit all the primary data to the residual viscosity, $\Delta\eta(\rho, T)$ term. Symbolic regression is a type of genetic programming that allows the exploration of arbitrary functional forms to regress data. The functional form is not known ahead of time, it is constructed during the fitting process by use of a set of operators, parameters, and variables as building blocks. Most recently this method has been used to obtain correlations for the viscosity of R161 [26], *n*-undecane [28], R1234yf and R1234ze(E) [27], ammonia [33], xenon [34], ethane-1,2-diol [35], and propane-1,2-diol [36]. We restricted the operators to the set (+, -, *, /) and the operands (constant, T_r , ρ_r), with $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$. As mentioned earlier, the critical temperature $T_c = 374.21$ K and critical density $\rho_c = 511.9$ kg m⁻³ are from the equation of state of Tillner-Roth and Baehr [64]. In addition, we adopted a form suggested by the hard-sphere model of Assael *et al.* [71], $\Delta\eta(\rho_r, T_r) = (\rho_r^{2/3} T_r^{1/2}) F(\rho_r, T_r)$. The symbolic regression method was used to determine the functional form for $F(\rho_r, T_r)$. The primary data were weighted according to the inverse value of their uncertainty squared. Additional weight was also applied to data at densities between 200 and 900 kg m⁻³ to compensate for the paucity of points in that region. For this task, the dilute-gas limit and the initial density dependence

term were calculated for each experimental point, employing Eqs. 2-6, and subtracted from the experimental viscosity to obtain the residual term, $\Delta\eta(\rho_r, T_r)$. The density values were obtained from the equation of state of Tillner-Roth and Baehr [64]. The final equation obtained was

$$\Delta\eta(\rho, T) = (\rho_r^{2/3} T_r^{1/2}) \left\{ c_0 + c_1 \rho_r + c_2 \frac{\rho_r^4}{T_r} + c_3 \frac{\rho_r^{14}}{T_r^2} \right\} \quad (7)$$

Coefficients c_i are given in Table 4, and $\Delta\eta$ is in $\mu\text{Pa s}$.

Table 4 Coefficients c_i for Eq. 7

i	c_i ($\mu\text{Pa s}$)
0	$-1.9049809 \times 10^{-1}$
1	1.4914096×10^1
2	2.1132461
3	1.8611635×10^{-5}

2.4 Comparison with data

Table 5 presents comparisons of the primary data with the correlation. The percent, or relative deviation is defined as $\text{PCTDEV} = 100(\eta_{\text{exp}} - \eta_{\text{fit}})/\eta_{\text{fit}}$, where η_{exp} is the experimental value of the viscosity and η_{fit} is the value calculated from the correlation. The average absolute relative deviation (AAD) is found using $\text{AAD} = (\sum |\text{PCTDEV}|)/n$, where the summation is over all n points, and the bias percent is found with the expression $\text{BIAS} = (\sum \text{PCTDEV})/n$. The average absolute relative deviation of the fit for all primary data up to the limit of the EOS, 70 MPa, is 1.09 %, with a bias of -0.09 %. At the 95 % confidence level, the relative uncertainty of the correlation from the 213 K up to 438 K and 70 MPa is 3.5 %. The correlation behaves in a physically realistic manner at pressures up to 400 MPa, keeping in mind that the equation of state where the density values are obtained is validated only up to 70 MPa. For regions where there were no data available for comparison, the uncertainties may be larger.

Table 5 Evaluation of the 1,1,1,2-tetrafluoroethane viscosity correlation for the primary data

Investigators/Reference	Publ. Year	AAD (%)	BIAS (%)
Vogel and Bich [25]	2021	0.03	0.00
Alam et al. [43]	2018	1.88	-1.85

Meng et al. [44]	2013	1.70	-1.69
Laesecke and Bair [24]	2011	1.78	0.04
Kumagai and Yokoyama [45]	2000	0.46	-0.20
Oliveira and Wakeham [46]	1999	4.88	4.88
Shibasaki-Kitakawa et al. [19]	1998	0.58	-0.21
Assael and Polimatidou [47]	1997	0.73	-0.27
Pàdua et al. [48]	1996	2.37	2.25
Heide [49]	1996	1.02	-0.52
Dunlop [20]	1994	0.22	0.22
Pasekov and Ustyuzhanin [21]	1994	0.30	0.05
Assael et al. [50]	1994	1.22	1.22
Dowdell and Matthews [11]	1993	0.39	0.33
Oliveira and Wakeham [12]	1993	0.76	0.56
Okubo et al. [13]	1992	1.99	-1.63
Ruvinskij et al. [7]	1990	1.59	-0.44
Entire Data Set*		1.20	-0.12

*Includes data in the extrapolation region 70 MPa – 400 MPa

Fig. 5 shows the percentage deviations of all primary viscosity data of 1,1,1,2-tetrafluoroethane from the values calculated by Eqs. 1 - 7, as a function of temperature, while Figs. 6 and 7 show the same deviations but as a function of the pressure and the density. The deviations of the experimental data from the present correlation are mostly within the uncertainty of the correlation, with the notable exception of the gas-phase viscosity measurements of Oliveira and Wakeham [46] at saturation which deviate by 4.88 % from the present correlation (however there is very good agreement with other measurements of the same group [12]).

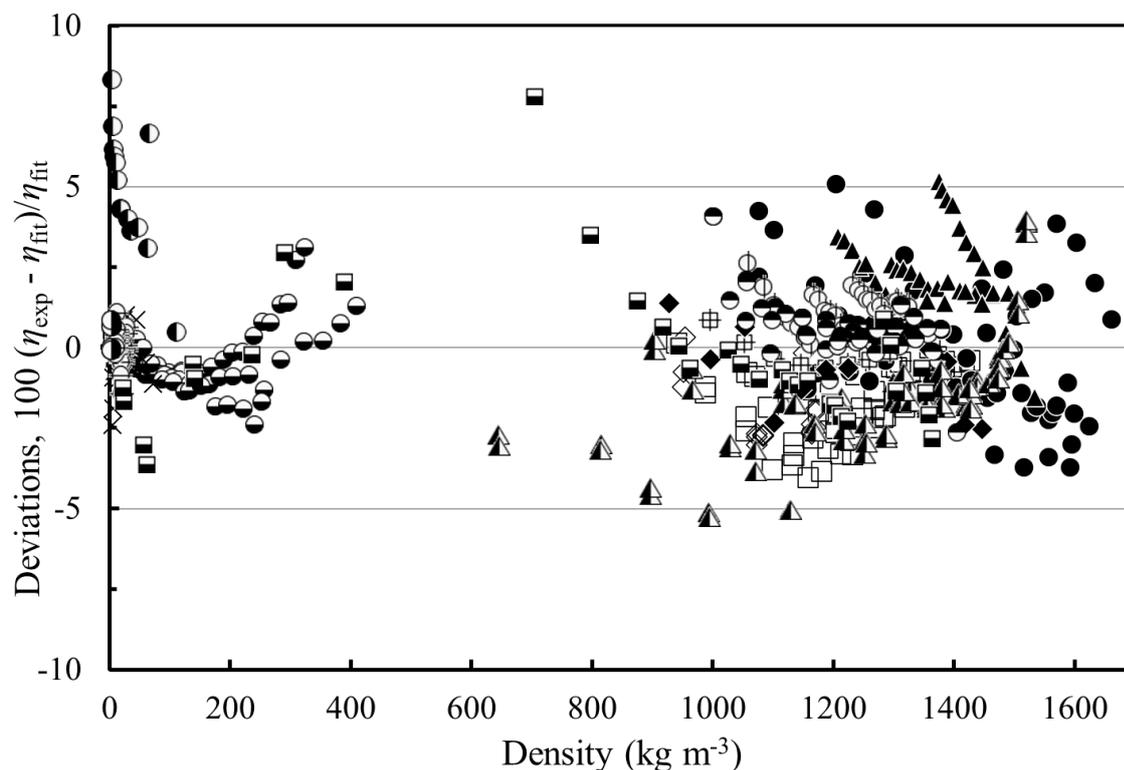


FIG. 7 Percentage deviations of primary experimental data of 1,1,1,2-tetrafluoroethane from the values calculated by the present model as a function of density. Vogel and Bich [25] (+), Alam et al. [43] (◇), Meng et al. [44] (□), Laesecke and Bair [24] (●), Kumagai and Yokoyama [45] (■), Oliveira and Wakeham [46] (⊙), Shibasaki-Kitakawa et al. [19] (⊖), Assael and Polimatidou [47] (X), Pàdua et al. [48] (▲), Heide [49] (◆), Dunlop [20] (*), Pasekov and Ustyuzhanin [21] (⊕), Assael et al. [50] (⊖), Dowdell and Matthews [11] (⊙), Oliveira and Wakeham [12] (⊙), Okubo et al. [13] (▲), Ruvinskij et al. (■).

Table 6 shows the average absolute percent deviation (AAD) and the bias for the secondary data. Finally, Fig. 8 shows a plot of the viscosity of 1,1,1,2-tetrafluoroethane as a function of the temperature for different pressures. The plot demonstrates the extrapolation behavior at pressures higher than the 70 MPa limit of the equation of state.

Table 6 Evaluation of the 1,1,1,2-tetrafluoroethane viscosity correlation for the secondary data

Investigators/Reference	Publ. Year	AAD (%)	BIAS (%)
Miyara et al.[43]	2018	1.85	-1.85
Zhao et al. [51]	2014	1.62	0.34
Meng et al.[44]	2011	1.69	-1.59
Comuñas et al. [52]	2003	6.60	6.60
Fröba et al. [53]	2000	2.24	1.52
Laesecke et al. [54]	1999	1.01	0.35
Pàdua et al.[48]	1996	10.75	10.75
Han et al. [55]	1995	2.39	1.56
Geller et al. [56]	1994	7.12	5.76
Burke et al. [57]	1994	6.42	6.42
Diller et al. [5]	1993	6.57	6.57
Bivens et al. [58]	1993	5.14	4.12
Ripple and Matar [59]	1993	3.06	3.06
Belyaeva et al. [60]	1993	1.18	0.00
Nabizadeh and Mayinger [6]	1992	4.78	4.78
Lavrachenko[61]	1992	1.16	-0.88
Heide and Lippold [62]	1990	10.20	10.20
Shankland et al. [9]	1988	9.89	9.89

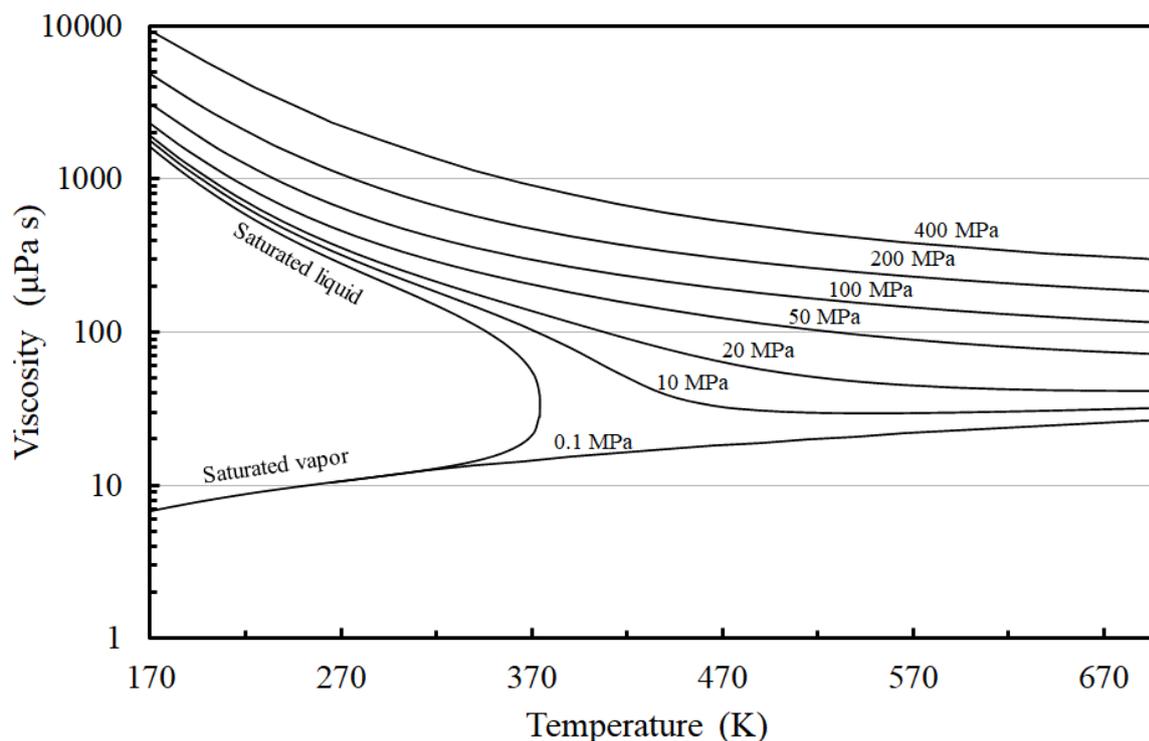


FIG. 8 Viscosity of 1,1,1,2-tetrafluoroethane as a function of the temperature for different pressures

2.5 Uncertainty estimates

As mentioned in Section 2.4, the average absolute relative deviation of the fit for all primary data at pressures to 70 MPa is 1.09 %, with a bias of -0.09 %. At the 95 % confidence level, the relative uncertainty of the correlation from 213 K up to 438 K and 70 MPa is 3.5 % based on comparisons with all primary data up to 70 MPa. However, it may be useful to examine specific regions and provide more detailed estimates of the uncertainties in various subregions, and to provide uncertainty estimates in the extrapolation region up to 400 MPa., the limit of the experimental data. Figure 9 summarizes estimates of the uncertainty of the correlation based on comparisons with the data sets with lowest uncertainty in the given regions. The uncertainty is lowest, 0.2 % - 0.3 %, in the low-density gas phase where we incorporated the recent work of Vogel and Bich [25]. According to Vogel and Bich [25] the uncertainty is 0.2 % near room temperature, increasing to 0.3 % at higher temperatures. Outside of the low-density gas region the uncertainty is larger. It is as high as 4 % in the very high-pressure region where only the data of Laesecke and Bair [24] are available for comparison. The estimated uncertainty along the saturation boundary in the liquid phase is 2.5 % and in the gas phase is 2 %. Note that any estimates for regions beyond the recommended region of applicability of the equation of state, 70 MPa, may have additional uncertainty due to the extrapolated density and should be re-evaluated if an updated equation of state becomes available in the future.

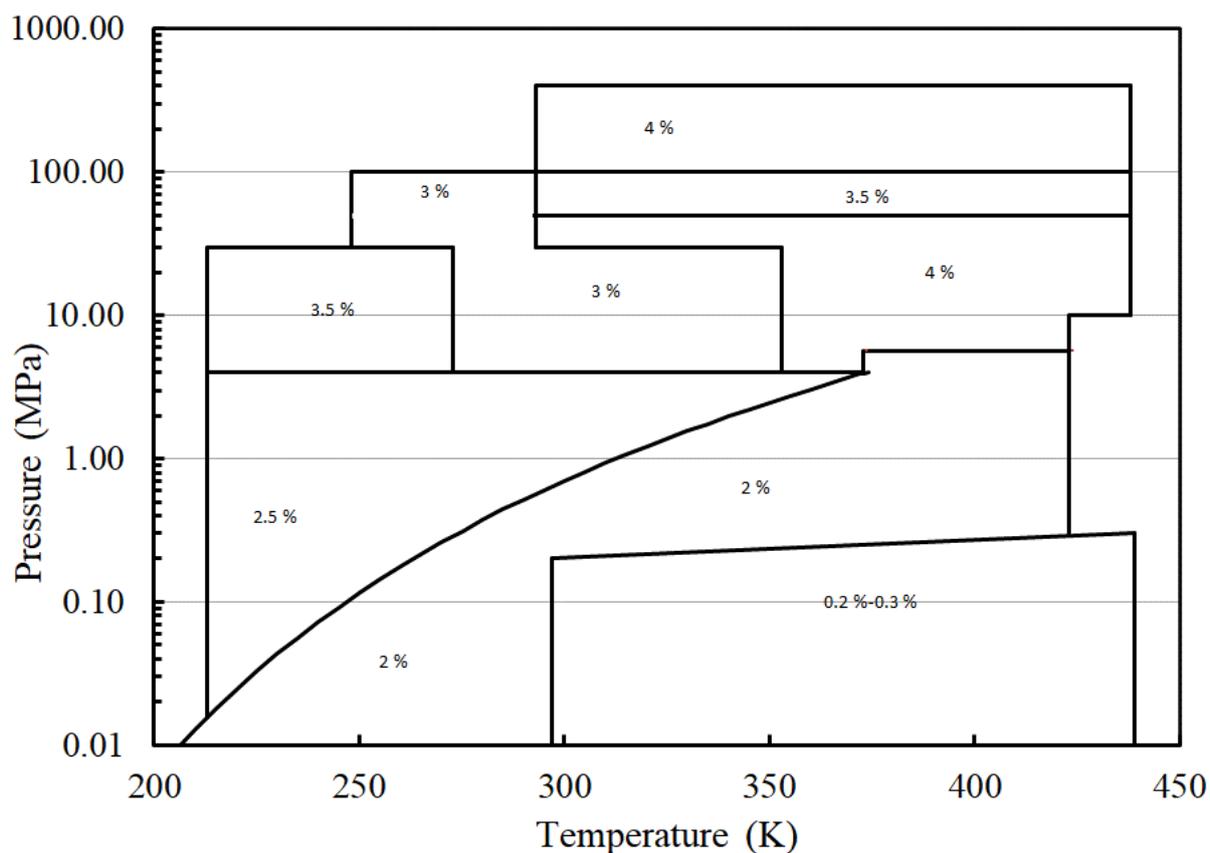


FIG. 9 Uncertainty estimates for the correlation

3 Recommended Values

In Table 7, viscosity values are given along the saturated liquid and vapor lines, calculated from the present proposed correlations between 170 and 370 K, while in Table 8 viscosity values are given for temperatures between 170 and 430 K at selected pressures. Saturation pressure and saturation density values for selected temperatures, as well as the density values for the selected temperature and pressure, are obtained from the equation of state of Tillner-Roth and Baehr [64]. The calculations are performed at the given temperatures and densities. For computer verification of values, the following points may be used for the given T , ρ conditions: $T = 350$ K, $\rho = 0.0$ kg m⁻³, $\eta = 13.77874$ μ Pa s; $T = 350$ K, $\rho = 100.0$ kg m⁻³, $\eta = 14.70183$ μ Pa s; $T = 350$ K, $\rho = 1000.0$ kg m⁻³, $\eta = 107.98464$ μ Pa s.

Table 7 Viscosity values of 1,1,1,2-tetrafluoroethane along the saturation line, calculated by the present scheme

T (K)	p (MPa)	ρ_{liq} (kg m ⁻³)	ρ_{vap} (kg m ⁻³)	η_{liq} (μPa s)	η_{vap} (μPa s)
170	3.9617×10^{-4}	1590.7	0.028625	1627.8	6.76
190	2.8170×10^{-3}	1537.5	0.18259	1040.6	7.56
210	1.2910×10^{-2}	1483.1	0.76222	702.2	8.35
230	4.3287×10^{-2}	1426.8	2.3660	498.0	9.12
250	1.1561×10^{-1}	1367.9	5.9546	368.6	9.86
270	2.6082×10^{-1}	1305.1	12.908	281.4	10.61
290	5.1805×10^{-1}	1236.8	25.187	218.6	11.39
310	9.3339×10^{-1}	1159.9	45.786	170.0	12.29
330	1.5599	1069.1	80.094	129.8	13.48
350	2.4611	951.32	140.99	93.93	15.44
370	3.7278	740.32	293.90	55.12	21.04

Table 8 Viscosity values of 1,1,1,2-tetrafluoroethane at selected temperatures and pressures, calculated by the present scheme

p (MPa)	T (K)	ρ (kg m ⁻³)	η (μ Pa s)	p (MPa)	T (K)	ρ (kg m ⁻³)	η (μ Pa s)
0.1	170	1590.8	1628.9	50	200	1575.7	1269.5
	200	1510.6	849.7		230	1510.7	772.7
	230	1426.9	498.3		260	1446.5	518.6
	260	4.8874	10.28		290	1383.0	377.1
	290	4.3289	11.47		310	1340.8	315.4
	310	4.0291	12.24		340	1278.0	250.6
	340	3.6548	13.40		370	1215.5	205.7
	370	3.3473	14.53		400	1153.7	173.0
	400	3.0891	15.66		430	1092.8	148.3
	430	2.8689	16.77				
10	180	1576.9	1405.9	70	205	1586.0	1326.4
	200	1525.7	930.2		230	1535.5	888.8
	230	1447.4	552.1		260	1476.1	598.7
	260	1365.8	361.6		290	1418.1	436.5
	290	1278.5	253.3		310	1380.1	366.2
	310	1215.4	203.8		340	1324.1	292.9
	340	1109.0	147.6		370	1269.4	242.9
	370	979.1	104.0		400	1216.1	206.9
	400	806.6	68.69		430	1164.2	179.9
	430	590.9	44.14				
30	185	1587.8	1474.0				
	200	1552.5	1096.7				
	230	1482.0	660.9				
	260	1411.1	440.4				
	290	1339.1	317.1				
	310	1290.3	262.9				
	340	1215.4	204.7				
	370	1138.2	163.5				
	400	1058.8	132.9				
430	978.4	109.9					

4 Conclusions

A new wide-ranging correlation for the viscosity of 1,1,1,2-tetrafluoroethane was developed based on critically evaluated experimental data and theoretical results. In the dilute-gas range, it incorporates the very recent correlation of Vogel and Bich [25] with a quoted uncertainty of 0.2 % to 0.3 % depending on the temperature, an initial-density dependence viscosity based on the scheme proposed by Vogel et al. [69], and an empirical residual term based on a critically evaluated set of measurements. The correlation has an estimated uncertainty of that ranges from a low of 0.2 % to a high of 4.0 % (at the 95% confidence level), depending on the temperature and pressure. It is valid from the triple point to 438 K, at pressures up to 70 MPa, a limit imposed by the validity range of the equation of state of Tillner-Roth and Baehr [64]. The correlation behaves in a physically realistic manner at pressures up to 400 MPa (the limit of the experimental data) and we feel the correlation may be extrapolated to this limit, although the uncertainty may be larger than the estimates given here, and caution is advised.

Supporting Information Available

A text file containing the parameters for the correlation is available for use with the REFPROP [22] computer program. It must be named R134a.fld. We thank Dr. Eric Lemmon of NIST for assistance developing this file.

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