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Reference Correlation for the Viscosity of Liquid Cyclopentane from 220 to 310 K at Pressures to 25 MPa

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A correlation in terms of temperature and molar volume is recommended for the viscosity of liquid cyclopentane as a reference for low-temperature, high-pressure viscosity measurements. The temperature range covered is from 220 to 310 K and the pressure range from atmospheric up to 25 MPa. The standard deviation of the proposed correlation, within a 95% confidence limit, is 1%.

KEY WORDS: density; pressure; reference; cyclopentane; viscosity.

1. INTRODUCTION

In 1986, following the recommendations of the International Association for the Properties of Water and Steam, water became one of the first viscosity reference fluids [1], in addition to various oils employed in different countries. The use of water in viscometry is, however, hindered by the fact that it is a polar liquid and, hence, unsuitable in certain viscometers. Furthermore, its application (at atmospheric pressure) is restricted to temperatures above 273.15 K.

Hence, over the last two decades the Subcommittee of Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry has undertaken the responsibility of examining other

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liquids for use as viscosity reference fluids. Thus, in addition to the recommended values for the viscosity of water [1, 2], in 1994 values for the viscosity of *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane [3] at various temperatures above 273.15 K and at atmospheric pressure were also recommended.

As the need for high-pressure and low-temperature viscosity reference fluids became apparent, in 2001 a reference correlation for the viscosity of liquid toluene from 213 to 373 K and at pressures up to 250 MPa was published [4] under the auspices of the Subcommittee of Transport Properties. Standard reference data for the thermal conductivity of liquid toluene had already been established [5]. Hence, another viscosity reference liquid below 273.15 K was proposed.

The formulation of the viscosity of cyclopentane over the temperature range 220 to 310 K and at pressures up to 25 MPa proposed in this paper, undertaken also under the guidance of the Subcommittee of Transport Properties (known as International Association for Transport Properties since 2001), aims to propose a second low-temperature viscosity reference liquid.

2. DENSITY

Since the proposed viscosity correlation is a function of temperature and density, a density formulation covering the whole temperature and pressure range was necessary. The density was calculated by a Strobridge equation of state, reported by Baonza et al. in 1992 [6]. This equation of state covers the temperature range from 193 to 298 K for pressures up to 104 MPa with an uncertainty of better than 0.06%. The Strobridge equation of state is

$$\begin{aligned} P = {} & RT\rho + (A_1 RT + A_2 + A_3/T + A_4/T^2 + A_5/T^4)\,\rho^2 \\ & + (A_6 RT + A_7)\,\rho^3 + A_8 T \rho^4 \\ & + (A_9/T^2 + A_{10}/T^3 + A_{11}/T^4)\exp(A_{16}\rho^2)\,\rho^3 \\ & + (A_{12}/T^2 + A_{13}/T^3 + A_{14}/T^4)\exp(A_{16}\rho^2)\,\rho^5 + A_{15}\rho^6 \end{aligned} \tag{1}$$

In this equation, P is the pressure (MPa), T is the temperature (K), ρ is the molar density ($\mathrm{mol \cdot dm^{-3}}$), and $R = 0.00831451\ \mathrm{MPa \cdot dm^3 \cdot K^{-1} \cdot mol^{-1}}$. The coefficients A_k are shown in Table I. The molar mass of cyclopentane has been taken equal to $70.134\ \mathrm{g \cdot mol^{-1}}$.

Table I. Coefficients A_k of Eq. (1)

k	A_k	
1	-0.40467×10	$\mathrm{dm^3 \cdot mol^{-1}}$
2	-0.84828×10	$\mathrm{MPa \cdot dm^6 \cdot mol^{-2}}$
3	-0.13843×10^4	$\mathrm{MPa \cdot dm^6 \cdot K \cdot mol^{-2}}$
4	0.85344×10^5	$\mathrm{MPa \cdot dm^6 \cdot K^2 \cdot mol^{-2}}$
5	-0.33052×10^9	$\mathrm{MPa \cdot dm^6 \cdot K^4 \cdot mol^{-2}}$
6	0.11647×10	$\mathrm{dm^6 \cdot mol^{-2}}$
7	0.53882	$\mathrm{MPa \cdot dm^9 \cdot mol^{-3}}$
8	-0.54779×10^{-3}	$\mathrm{MPa \cdot dm^{12} \cdot K^{-1} \cdot mol^{-4}}$
9	-0.16600×10^8	$\mathrm{MPa \cdot dm^9 \cdot K^2 \cdot mol^{-3}}$
10	0.40090×10^{11}	$\mathrm{MPa \cdot dm^9 \cdot K^3 \cdot mol^{-3}}$
11	-0.11728×10^{14}	$\mathrm{MPa \cdot dm^9 \cdot K^4 \cdot mol^{-3}}$
12	-0.52554×10^6	$\mathrm{MPa \cdot dm^{15} \cdot K^2 \cdot mol^{-5}}$
13	0.44522×10^8	$\mathrm{MPa \cdot dm^{15} \cdot K^3 \cdot mol^{-5}}$
14	0.52947×10^{11}	$\mathrm{MPa \cdot dm^{15} \cdot K^4 \cdot mol^{-5}}$
15	0.27140×10^{-3}	$\mathrm{MPa \cdot dm^{18} \cdot mol^{-6}}$
16	-0.06750	$\mathrm{dm^6 \cdot mol^{-2}}$

3. VISCOSITY

3.1. Experimental Data

The data sets considered in the present formulation are shown in Table II. Nine different sets of measurements performed since 1937 were included [7–14]. The purity of each sample employed, the temperature range of the data set, the maximum pressure and method used, the number of points in the set, and the uncertainty in the viscosity measurements are also presented. Since only two sets of measurements exist at higher pressures [8, 10], and the pressure range of the one set [8] is limited to 25 MPa, this was taken as the highest pressure for the correlation.

Where high pressures or low temperatures are involved, the uncertainty is increased, and this higher uncertainty is indicated within parentheses. In the same table, the fluids employed for the calibration of each viscometer are shown. It should be pointed out that instruments calibrated with water are expected to produce more accurate measurements. For all these viscosity measurements, the density of cyclopentane at the experimental T and P was recalculated as described above. No correction to ITS 90 was considered necessary, as the five sets of measurements performed before 1990 employ a very limited temperature range in which the correction is negligible.

Table II. Experimental Data for the Viscosity of Liquid Cyclopentane

Year	First Author	Ref.	Min. Purity (%)	Method[c]	Calibration Fluid(s) Employed	Temperature range (K)	Max. Pressure[d] (MPa)	Number of data	Quoted Uncertainty[e] (%)	Deviations[f] Average (%)	Maximum (%)
					Primary Measurements						
1980	Levien	[7]	99.98	CF	water	298	0.1	1	0.5	0.1	0.1
2000	Assael	[8]	99.5[a]	VW	water, toluene	220–310	25	67	0.5 (1)	0.3	1.0
2002	Bauer	[9]	99.5	CF	standard oils	243–293	0.1	4	0.2	0.7	1.0
2002	Harris	[10]	99.5	CF	water, toluene, oils	278–298	0.1	5	0.5	0.3	0.6
2002	Harris	[10]	99.5	FB	water, toluene, oils	258–298	25[d]	56	2	0.5	1.6
					Secondary Measurements						
1937	Timmermans	[11]	99	CF	water	288, 303	0.1	2	1	1.3	1.3
1962	Khalilov	[12]	99	CF	water	293, 310	0.1	2	1.6	1.5	2.5
1969	Brazier	[13]	99	RB	silicone oils	303	0.1[d]	1	NA	0.8	0.8
1986	Fischer	[14]	99[b]	CF	water	290–310	0.1	Equation	0.2	2.0	3.0

[a] Treated with molecular sieves to remove water content.

[b] Further distilled under vacuum.

[c] CF: capillary flow; VW: vibrating wire; RB: rolling ball; FB: falling body.

[d] Ranges restricted to less than 25 MPa.

[e] At the lowest temperatures or highest pressures, the uncertainty is shown within parentheses.

[f] Refers to the percentage deviations of experimental values from the values calculated from Eqs. (2) and (3).

The measurements presented in Table II were separated into primary and secondary data, in the fashion adopted previously [5].

(a) Primary data are the results of measurements carried out with an instrument of high precision for which a complete working equation and a detailed knowledge of all corrections are available.

(b) Secondary data are the results of measurements which are of higher uncertainty than primary data. The higher uncertainty may arise from operation at extreme conditions or incomplete characterization of the apparatus.

Although the division of experimental data into these categories is somewhat subjective, the following recommendations [5] have been employed as a means of identifying primary data:

(i) A complete working equation for the instrument employed must be available. The form of the equation must be such that the sensitivity of the viscosity to the principal variables does not magnify the random errors of measurement.

(ii) All principal variables should be measurable to a high degree of precision.

(iii) Published work should include some description of purification methods and a guarantee of purity.

(iv) The data reported must be unsmoothed data in table form and not in graphs or fitted equations.

(v) Measurements should be performed in a way that uncertainties are clearly stated.

According to the above discussion, the measurements of Levien and Mills [7], Assael and Dalaouti [8], Bauer [9], and Harris et al. [10] were all considered as primary data, and the correlation was based on these data.

3.2. Correlation

Since the temperature and pressure ranges were wide, resulting in a range for the viscosity of cyclopentane of 350 to 1500 $\mu\text{Pa}\cdot\text{s}$, a correlation in temperature and pressure would not seem plausible. Hence, it was preferred to express the viscosity as a function of the temperature and density. In deriving the correlation, weights inversely proportional to the quoted uncertainties were employed.

Table III. Coefficients e_k of Eqs. (2) and (3)

K	e_k	
0	1.980210×10^{-2}	$\mathrm{mol\cdot cm^{-3}}$
1	0.1296134×10	$\mathrm{K^{0.5}\cdot \mu Pa^{-1}\cdot s^{-1}}$
2	-3.485304×10^{-2}	$\mathrm{K^{0.5}\cdot \mu Pa^{-1}\cdot s^{-1}\cdot mol\cdot cm^{-3}}$
3	2.358497×10^{-4}	$\mathrm{K^{0.5}\cdot \mu Pa^{-1}\cdot s^{-1}\cdot mol^{2}\cdot cm^{-6}}$
4	3.974536×10^{-2}	$\mathrm{cm^{3}\cdot mol^{-1}\cdot K^{-1}}$
5	-7.667145×10^{-5}	$\mathrm{cm^{3}\cdot mol^{-1}\cdot K^{-2}}$

Following a thorough optimization of all parameters involved, the viscosity, η ($\mu\mathrm{Pa\cdot s}$), can be obtained as a function of the absolute temperature T (K) as

$$\eta = \frac{\sqrt{T}\,(1+e_0V_\mathrm{r})}{(e_1+e_2V_\mathrm{r}+e_3V_\mathrm{r}^2)} \tag{2}$$

where

$$V_\mathrm{r} = V + e_4(T-T_\mathrm{r}) + e_5(T-T_\mathrm{r})^2. \tag{3}$$

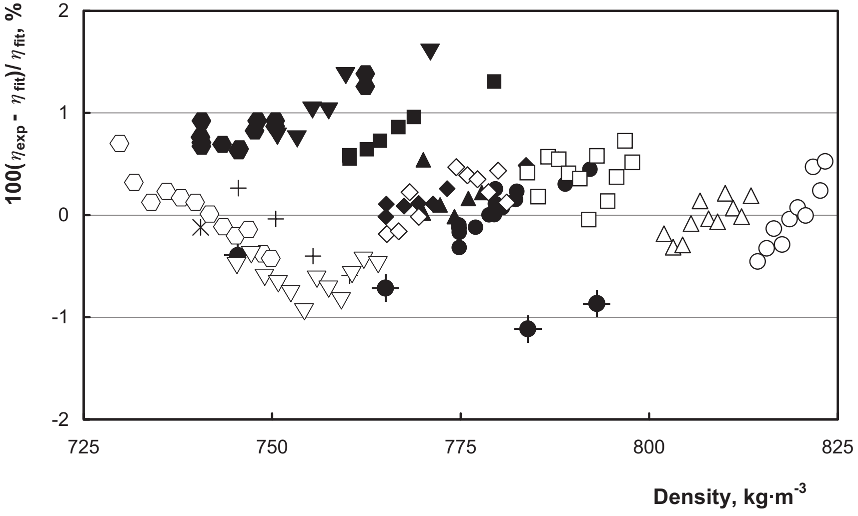

Fig. 1. Percentage deviations of the primary viscosity measurements as a function of the density from the values calculated with Eqs. (2) and (3). Levien and Mills [7]: (⁎); Assael et al. [8]: (○) 219 K, (△) 233 K, (□) 253 K, (◇) 273 K, (▽) 293 K, (⬡) 308 K; Bauer [9]: (⌖); Harris et al. [10]: (●) 260 K, (▲) 268 K, (◆) 273 K, (■) 278 K, (▼) 287 K, (⬢) 298 K, (+) capillary data at 0.1 MPa.

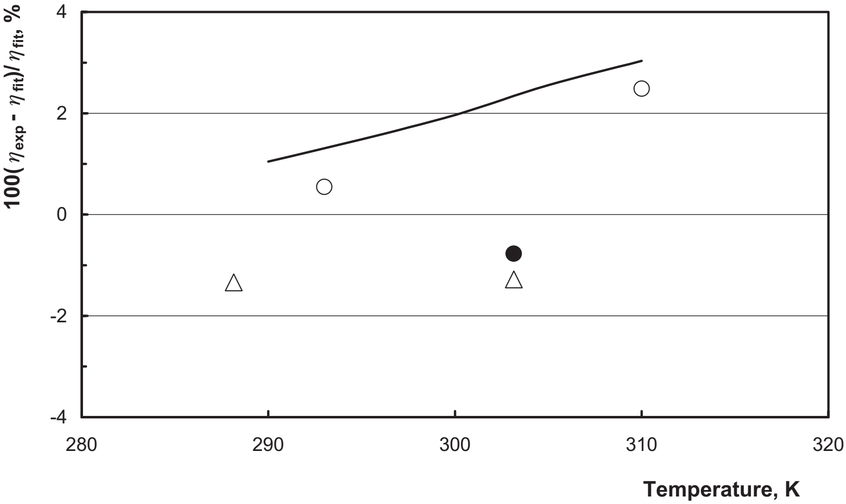

Fig. 2. Percentage deviations of the secondary viscosity measurements as a function of the temperature from the values calculated with Eqs. (2) and (3). Timmermans and Martin [11]: (△); Khalilov [12]: (○); Brazier and Freeman [13]: (●); Fischer and Weiss [14]: (——).

The reference volume, V_r ($\mathrm{cm^3 \cdot mol^{-1}}$), represents the molar volume V ($\mathrm{cm^3 \cdot mol^{-1}}$) at the reference temperature $T_r = 273.15$ K. The values of coefficients e_k are given in Table III. Equations (2) and (3) form a consistent scheme by which the viscosity can be calculated as a function of the temperature and density.

The deviations of all primary measurements from the proposed correlation are shown in Fig. 1, while in Table II the average and maximum deviations of each data set from the present correlation are shown as percentages. The standard deviation of the proposed correlation, within a 95%

Table IV. Recommended Values for the Viscosity of Liquid Cyclopentane

P (MPa)	ρ ($\mathrm{kg \cdot m^{-3}}$)	η (μPa · s)	ρ ($\mathrm{kg \cdot m^{-3}}$)	η (μPa · s)	ρ ($\mathrm{kg \cdot m^{-3}}$)	η (μPa · s)	ρ ($\mathrm{kg \cdot m^{-3}}$)	η (μPa · s)
	223.15 K		248.15 K		273.15 K		298.15 K	
0.1	810.9	1168	788.6	788	765.1	560	740.5	416
5	813.6	1215	791.8	821	769.0	585	745.1	435
10	816.3	1264	795.0	856	772.7	611	749.6	456
15	818.9	1314	798.1	891	776.3	637	753.8	476
20	821.4	1365	801.0	927	779.8	663	757.8	497
25	823.9	1417	803.9	963	783.1	690	761.6	517

confidence limit, is 1%. It can be noted that the deviations of the five data sets considered, are well within the combined uncertainties. In Fig. 2, the deviations of the secondary measurements from the proposed correlation are also shown. In this case, the deviations are larger and extend up to 3%.

In Table IV, recommended values for the viscosity of cyclopentane are given for pressures up to 25 MPa.

4. CONCLUSIONS

A correlation in terms of temperature and molar volume is recommended for the viscosity of liquid cyclopentane as a reference for low-temperature viscosity measurements. The temperature range covered is from 220 to 310 K, and the pressure range is from atmospheric up to 25 MPa. The standard deviation of the proposed correlation, within a 95% confidence limit, is 1%.

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