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The Viscosity of Liquid Water at Pressures up to 32 MPa[1]

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The paper reports new, preliminary measurements of the viscosity of liquid water along two isotherms as a function of pressure up to 32 MPa. The measurements have been performed with a vibrating-wire viscometer especially modified for the purpose. The instrument has been calibrated with respect to the viscosity of water at a pressure of 0.1 MPa and a temperature of 293.15 K, for which an accurate reference value is available. With due regard to the precision of the determination of individual quantities and the accuracy of the calibration data, it is estimated that the accuracy of the present results is one of ±0.3% under all conditions.

KEY WORDS: vibrating-wire viscometer; viscosity; water.

1. INTRODUCTION

Within his wide range of interests Professor Kestin included, since the 1950s, a very considerable attachment to the measurement of the viscosity of fluids. Indeed, he was, in common with others, fascinated by the fact that whereas the viscosity is such a seemingly simple property to measure, it has proved extremely difficult to achieve a high accuracy in the determinations. Thus, it is worthwhile to note that it was not until 1970 that measurements of the viscosity of gases at elevated temperatures were made with an accuracy of better than 1% and that then the success was achieved by Kestin himself with an oscillating-disk viscometer [1]. This achievement was the culmination of a period of development of the

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theory of the instrument and its design that extended over a period of approximately 12 years [2, 3]. Since the new measurements of Kestin and others [1, 3, 5] cast considerable doubt on the earlier measurements of the viscosity of gases by more conventional methods [6, 7], the formulation of the theory of the instrument and verification of its validity were of particular importance.

More or less concurrently, Kestin was involved with the International Association for the Properties of Steam, where, among other activities, he became particularly interested in the viscosity of water. The viscosity of this substance had been the subject of an intensive study at the then National Bureau of Standards [8] in order to determine a standard reference value at a temperature of 20°C. Kestin, together with others [9], debated the uncertainty that should be attached to this measurement and, subsequently, prepared a precise representation of the viscosity of liquid water under saturation conditions over a modest range of temperature. More recently, Kestin collaborated with Øye [10] on a new, absolute determination of the viscosity of water under the same conditions.

Prompted by these two interests of Kestin, we report in this paper new, relative measurements of the viscosity of liquid water over a range of pressures. We have chosen to employ for the measurements a vibrating-wire viscometer which was originally developed for measurements on liquid hydrocarbons [11, 12] and has subsequently been used for measurements on environmentally acceptable refrigerants [13]. In its early form, this type of instrument was much maligned owing to the fact that it lacked a rigorous working equation and a set of appropriate corrections. In particular, as Kestin has often commented, there had been no consideration of the importance of secondary flow in this instrument of the same kind as had been carried through for oscillating-body viscometers. Indeed, the theory of the instrument employed here [14] owes a considerable amount to the guidance of Kestin and the most recent measurements have demonstrated that it is capable of a precision of ±0.1% in the viscosity over a wide range of conditions. It is therefore particularly appropriate that we are able to employ the instrument in the current context.

2. EXPERIMENTS

2.1. The Viscometer

The gross features of the vibrating-wire viscometer employed for the present measurements have already been described [11]. However, the special characteristics of water make the detailed construction of the instrument used earlier inappropriate for measurements on such a fluid. For that reason, substantial modifications of the instrument have been necessary. Figure 1 contains a schematic diagram of the essential components of the vibrating-wire assembly. The vibrating wire itself is still made of tungsten, with a nominal diameter of 100 μm and a length of 6 cm. It is supported from the upper plate of the assembly in a 304 stainless-steel chuck (2), which grips a stainless-steel tube into which the wire is swaged. At the lower end the wire carries a stainless-steel weight (8) to which it is affixed by a similar chuck (7) and a tube. The magnetic field required to excite vibrations of the wire is provided by two samarium–cobalt magnets (3) supported in a cage (4) made of stainless steel. The two magnets are plated with an impervious gold layer to guard against chemical attack by water and are linked by a yoke made of a magnetic stainless steel in order to

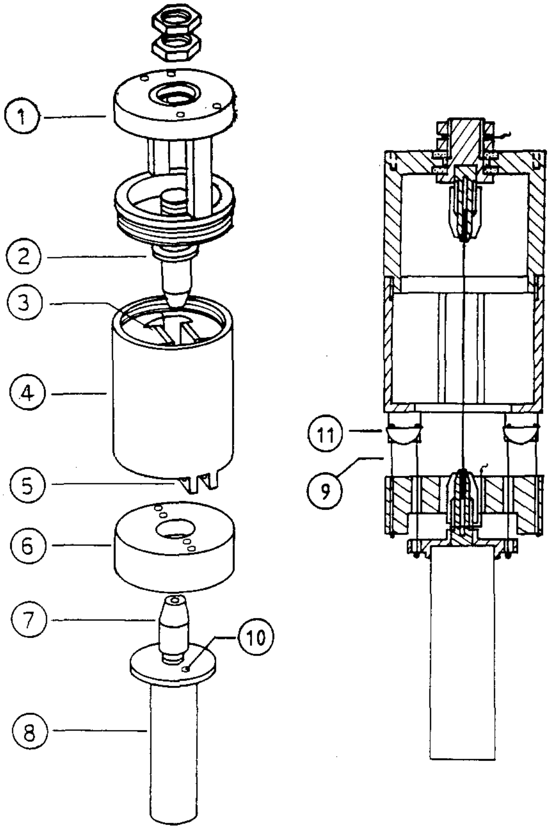

Fig. 1. The vibrating-wire assembly.

secure as high a magnetic field as possible. Considerable care was taken during the assembly of the viscometer to remove all of the loosely adhering particles of gold from the surface of the magnet since tests revealed that these were prone to detachment upon immersion in water and subsequent adherence to the vibrating wire.

The electrical connections to the upper and lower chucks of the vibrating wire were made with 0.5-mm-diameter 316 stainless-steel wire which was also used in the electrical feedthrough from the pressure vessel. A very fine nickel wire was employed to connect the lower chuck to provide a flexible coupling. All connections were made by spot-welding.

All of these precautions were found to be necessary to eliminate the dissimilar metals present in the earlier version of the instrument. It was found, during initial trials with the earlier version, that electrolytic action in the system caused particles of metal to be deposited preferentially on the tungsten wire. Typically, the particles found had a diameter of up to 20 μm, as revealed by scanning electron microscopy; energy dispersive spectroscopy confirmed that they arose from the solders employed in the assembly of the previous cells. The deposition of the particles had, of course, a very significant effect upon the damping characteristics of the wire so that apparent, time-dependent viscosities were observed as the extent of deposition increased.

Following the introduction of the assembly described, it was found that the reproducibility of the instrument under repeated cycling of temperature and pressure was one of $\pm 0.1\%$ over several weeks and was therefore approximately equal to the precision of measurements. Indeed, even if the vibrating-wire sample was exchanged with another sample from the same roll, the reproducibility remained of the same order. This is taken to be conclusive evidence that the wire remained uncontaminated during the measurements reported here.

The viscometer assembly shown in Fig. 1 is assembled inside a PTFE sleeve which serves to separate the test fluid on the inside from the pressurising hydraulic fluid filling an appropriate pressure vessel [11].

2.2. Working Equations

The present viscometer has been designed in accordance with the theory of the instrument so that all of the constraints upon the design are satisfied [14]. As a consequence, the working equation for the evaluation of the viscosity from the measured decrement, Δ, and frequency, ω, of the oscillation takes the form [14]

$$\Delta = \frac{(\rho/\rho_s)\,k' + 2\Delta_0}{2[1 + (\rho/\rho_s)\,k]} \tag{1}$$

where ρ is the fluid density and ρ_s that of the wire material. In addition, k and k' are given by

$$k = -1 + 2\mathrm{Im}(A) \tag{2}$$

and

$$k' = 2\mathrm{Re}(A) - 2\Delta\mathrm{Im}(A) \tag{3}$$

with

$$A = (i - \Delta)\left\{1 + \frac{2K_1(s)}{sK_0(s)}\right\} \tag{4}$$

and

$$s = [(i - \Delta)\,\Omega]^{1/2} \tag{5}$$

where

$$\Omega = \rho\omega R^2/\eta \tag{6}$$

and $K_{0,1}$ are modified Bessel functions. In addition, Δ_0 is the decrement of the oscillation *in vacuo*, which has been determined *in situ*, R the radius of the wire, and η the fluid viscosity.

In practice, only one correction to this working equation is significant for the present apparatus ($<0.01\%$) and that arises from the fact that the fluid is necessarily contained within a solid wall. A correction for this effect is available [14] and, in the present work, never amounts to more than 0.08%, so that its application introduces negligible error.

2.3. Precision

The precision of the viscosity measurements is determined by the uncertainty in the evaluation of the decrement of the oscillation, its frequency, and the density of the fluid. For the current work with water the error in the liquid density is sufficiently small as to be negligible by comparison with the uncertainty in Δ and ω. In general, the precision and reproducibility of the measurement of Δ are better than $\pm 0.1\%$, and that of ω two orders of magnitude better.

2.4. Calibration

The working equations, Eqs. (1) to (6), demonstrate that absolute measurements of the viscosity of a fluid also require a knowledge of the wire radius, R, and of the density of the wire material, ρ_s. Because these two quantities are inaccessible to direct measurement for the small sample of wire employed, it is preferable to make relative measurements in which these quantities are determined using standard reference values for the viscosity of a fluid.

In our previous work [11, 13, 15] the calibration has been carried out either with respect to toluene at two temperatures or with respect to toluene and four normal alkanes at one temperature. As has been mentioned previously, water could not be used for these calibrations because the instrument was incompatible with that fluid. The viscosities of the hydrocarbons listed above are known with an uncertainty of ±0.3% so that the measurements reported hitherto have been stated to have an accuracy of ±0.5–0.6%, which is considerably worse than their precision.

The present instrument allows the characteristics of the wire to be determined more accurately. Specifically, we can employ the standard reference value for the viscosity of water at 20°C and 0.1 MPa advocated by Kestin et al. [9], namely,

$$\eta = 1002.0\ \mu\mathrm{Pa}\cdot\mathrm{s} \tag{7}$$

for the calibration. This standard reference value has an uncertainty of ±0.1% so that it is possible to reduce the uncertainty in the viscosity measurements over the entire range of conditions studied here to one of ±0.3%.

In practice, to carry out this calibration we have employed the value of density of the tungsten wire determined earlier [11], $\rho_s = 19{,}090\ \mathrm{kg}\cdot\mathrm{m}^{-3}$, and used a single calibration with water at 20°C and 0.1 MPa to determine R. In this way we obtained

$$R = 49.95\ \mu\mathrm{m} \tag{8}$$

which is to be compared with that determined earlier in the hydrocarbon systems [11]

$$R = 49.90\ \mu\mathrm{m} \tag{9}$$

The difference of 0.1% in these two values is entirely consistent with the stated uncertainty in the reference value employed for the viscosity of toluene, and both are consistent with a direct determination of the diameter of the wire with an optical microscope, which gave

$$R = 50.0 \pm 0.5\ \mu\mathrm{m} \tag{10}$$

These results provide considerable support for the compatibility of the instrument and the theory of it.

2.5. Materials

The water employed for the present measurements was doubly distilled and deionized before use. Its electrical conductivity was checked before and after use and found in both cases to be 1.3 $\mu S \cdot cm^{-1}$. The density of water required for the evaluation of the viscosity has been taken from the work of Sengers and Watson [16].

3. RESULTS

The present results represent the first stage of a systematic investigation of the viscosity of water and aqueous solutions. Since the viscosity of water is known with rather greater accuracy at the saturation vapor pressure than under elevated pressures, we have carried out two series of measurements. Table I contains the results of measurements along the saturation line in the temperature range 20 to 40°C. The table includes the results of the special correlation of critically evaluated experimental data for calibration purposes given by Kestin et al. [9] and the deviations between the two sets of results. The greatest deviation amounts to 0.19% and is therefore consistent with the mutual uncertainty of the two sets of data.

Table II contains the results of measurements of the rather weak pressure dependence of the viscosity of liquid water at two nominal temperatures, 298.15 and 313.15 K. These two isotherms have been selected in this preliminary study since the pressure dependence of the viscosity is of opposite sign in the two cases. Corrections from the experimental temperature to the nominal temperature have been made with the aid of the IAPS representation of the viscosity of water and do not amount to more than 0.4%, so that the application of the correction introduces a negligible additional error.

Figure 2 displays the deviations between the present experimental data

Table I. The Viscosity of Liquid Water Along the Saturation Line

Temperature (K)	Density ($kg \cdot m^{-3}$)	Experimental viscosity ($mPa \cdot s$)	Reference viscosity [9] ($mPa \cdot s$)	Deviation (%)
293.11	998.2	1.0032	1.0030	+0.02
297.96	997.1	0.8944	0.8939	+0.06
303.75	995.5	0.7862	0.7871	−0.12
307.97	994.1	0.7223	0.7217	+0.08
312.90	992.3	0.6547	0.6560	−0.19

Table II. Viscosity of Liquid Water as a Function of Pressure

Pressure (MPa)	Temperature (K)	Density ($kg \cdot m^{-3}$)	η_{expt} ($mPa \cdot s$)	$\eta(T_{nom}), P$ ($mPa \cdot s$)
		$T_{nom} = 298.15$ K		
0.10	297.96	997.1	0.8944	0.8906
5.27	298.04	999.4	0.8927	0.8905
10.54	298.05	1001.8	0.8920	0.8899
15.50	298.04	1003.9	0.8904	0.8882
21.37	298.03	1006.5	0.8896	0.8873
24.62	298.02	1007.9	0.8882	0.8857
		$T_{nom} = 313.15$ K		
0.10	312.90	992.3	0.6547	0.6516
5.17	312.91	994.5	0.6545	0.6516
10.23	312.91	996.7	0.6552	0.6522
15.50	312.88	999.0	0.6545	0.6512
20.46	312.84	1001.1	0.6566	0.6529
25.53	312.79	1003.2	0.6578	0.6535
32.01	312.71	1005.9	0.6590	0.6537

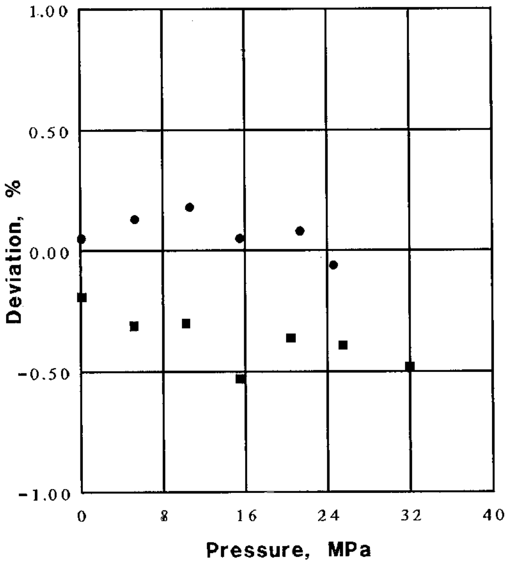

Fig. 2. Deviations of the present experimental data for the viscosity of water from the IAPS representation of the property 16 as a function of pressure. (●) 298.15 K; (■) 313.15 K.

for the viscosity of water and the correlation recommended by IAPS [16]. The IAPS recommendation is a weighted fit of previous measurements in the range of conditions of interest here and therefore provides a convenient basis for comparison. The IAPS formulation has an uncertainty of ±1.0% in the range of interest so that the degree of agreement shown is satisfactory.

4. DISCUSSION

A vibrating-wire viscometer has been designed and constructed for operation with liquid water over a modest temperature range above ambient at pressures up to 30 MPa. An accuracy of ±0.3% is estimated for the preliminary measurements reported and it is expected that this can be maintained over a much wider range of conditions.

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