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Reviews

Metrology of Viscosity: Have We Learned Enough?[†]

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Viscosity is one of the most important properties for many technological and scientific applications, and therefore it has been the subject of an enormous effort of measurement, correlation, and interpretation. This effort is completely inconsistent with the fact that it is probably the fluid property with less independent reference values that can be used by most of the everyday users as guidance, calibration, or designing tools. The only accepted standard, the viscosity of pure water at 20 °C, is unsatisfactory because the viscosity among different fluids can vary by a factor of 10^{14}. Its application in the current step-up procedures to produce certified reference materials of higher viscosity, although useful for industrial purposes, degrades the desired small uncertainty of these values. An analysis of the metrology status for Newtonian liquids viscosity, including the best available measurement methods, applicable ranges, existing reference data, uncertainties, and traceability of the measurements to the SI, is made. The discussion assumes in general the internationally accepted definitions of uncertainty.

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1. Introduction

Viscosity played a key role in the work of Robin Stokes, especially in the theory and experiment in electrolyte solutions, when its relations with diffusion of ions and the electrical conductivity of weak and strong electrolytes were fundamental to understand ion mobility in the liquid state.[1] His contribution to study the transport of mass, momentum, and electrical current in liquid systems paved the way to study the transport properties of ionic liquids and low and high temperature molten salts. It is one of the most important properties for many technological and scientific applications, and therefore it has been the subject of an enormous effort of measurement, correlation, and interpretation.

Metrology, the science of measurement, includes all theoretical and practical aspects of measurement, whichever the measurement uncertainty and field of application. It includes the range of fluid states of the measurand (viscosity in the present case), the selection of the best available methods of measurement, existing standards (reference fluids with recommended values of viscosity at specified states), traceability chain, measurement procedures, and uncertainty estimation.

Notwithstanding the efforts by Robin Stokes and others, the metrology of viscosity evidences a particularly striking lack of independent reference values available to the everyday user, as calibration standards or as guidance for design tools. From the end-user point of view, the only viscosity reference point accepted so far is the viscosity of pure water[2] at 20 °C and 0.1 MPa,[3] as recommended by ISO/TR 3666:1998(E)[4] and accepted by IUPAC and OIML (International Organization for Legal Metrology, http://www.oiml.org). The existence of just this single reference point seems to be quite unsatisfactory, as the viscosity of fluids can vary by a factor of 10^{14}. This point has based all the recommendations by metrological laboratories all around the world on sets of other calibrating fluids, obtained with the step-up procedure in capillary viscometry, in the form of certified reference materials (CRMs), like different kinds of oils, polyisobutenes, and glasses.[5]

Many reasons may certainly be found, at an international level, to explain this situation, but the most important seems to be the fact that, up to now, it has not been possible to establish a primary method of measurement for viscosity or a set of primary methods for the different ranges of viscosity. In fact, the word metrology implies not only the existence of standards, traceable to SI,[6] but also the existence of accepted methods of measurement, capable of realizing the units and the targeted quantities to be measured (measurands), and capacity to calculate the uncertainty of the data obtained.[7]

The experimental methods used for the measurement of viscosity can be classified as absolute and relative. In the absolute methods, the measured value of the viscosity must be defined precisely in terms of the measurement parameters (the so-called working equation corresponding to a well-defined model of the experimental measurement). Furthermore, the quality of the working equation (i.e., the accuracy of the description of the measurement and of its departures from all the idealizations involved), as well as the uncertainty of the principal measurement parameters, must be subjected to an unambiguous assessment. This statement is conceptually identi-

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cal to the definition of primary methods by CCQM (Comité Consultatif pour la Quantité de Matière - BIPM - http://bipm/org/en/committees/cc/ccqm) in 1995: A primary method of measurement is a method having the highest metrological qualities, the operation of which can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units, and whose results are, therefore, accepted without reference to a standard of the quantity being measured.

Following the strategy developed by CCQM, a hierarchy of methods can be established such that a primary method is used to validate or calibrate a secondary method which, in turn, can be directly linked to a working level method. Whereas the primary method will often be expensive and time-consuming, a typical working level method will be simple but more uncertain. Traceability to the SI requires that the measurements be made using a primary method of measurement, which is correctly applied and stated with an evaluated uncertainty. However, if the primary method is not available, other indirect methods can be used, including combinations of methods that are not established as primary, but have calculated uncertainties, or by comparison with reference materials of the same or similar substance or mixture, which have values accepted by the international community and can be linked to the SI through a chain of other comparisons.

The viscosity of a fluid is a measure of its tendency to dissipate energy when it is perturbed from equilibrium by a force field, which distorts the fluid at a given rate. The viscosity depends on the thermodynamic state of the fluid, and it is usually specified by pairs of variables, temperature, and pressure (T, P) or temperature and density (T, ρ) for a pure fluid, to which must be added a composition dependence in the case of mixtures. The dissipative mechanism of shear creates, inevitably, local temperature gradients, which can alter slightly the reference thermodynamic state to which the measurement is assigned, from the initial, unperturbed, equilibrium state. Because it is impossible to measure local shear stresses, the measuring methods must be based on some integral effect, amenable to accurate measurements, from which, by averaging, the reference state is obtained. In addition to the general constraints already referred for primary instruments, we must require that the rates of shear are small enough to maintain a near equilibrium state and that hydrodynamic stability is maintained. Disregarding one or more of these constraints may be responsible for severe errors of measurement, a fact that has not been acknowledged by many previous publications.

It is the purpose of this paper to analyze the current situation of best available experimental methods and the references for the measurement of viscosity, with special emphasis on the fluids, ranges, and uncertainties. It is assumed that all measurements made are traceable to the SI. The discussion assumes in general the definitions of uncertainty accepted internationally and reported by Taylor and Kuyatt, with a coverage factor $k = 2$.[7] The philosophy followed in the academic world is different from that of metrological institutions, making it sometimes difficult to conciliate both forms of dealing with the problem.

2. Methods of Measurement

Strictly speaking, there is no primary method at present for the measurement of the viscosity of liquids because the absolute methods developed so far, to achieve high accuracy, involve the use of instrumental parameters obtained through calibration. However, the analysis of such methods[8,9] (designated as relative or secondary) shows a large range of levels of departure from the accepted definition of a primary method. Therefore, we chose to designate as "quasi-primary" any method for which a physically sound working equation, relating the viscosity to the experimental-measured parameters, is available but where the values of some of these parameters must be obtained by an independent calibration with a known standard. Among the existing methods of measurement of viscosity, we can consider as "quasi-primary" the oscillating body (disk, cup, or sphere), the vibrating wire, the torsionally oscillating quartz crystal, and surface light scattering spectroscopy (SLS) methods. Recently, an attempt has been made to develop a viscometer based on the falling-ball operating in an absolute way, which is close to our concept, as it uses very low Reynolds numbers ($Re < 1.4$).[10] In the oscillating disk viscometer, the disk's edge effect must be calibrated. In the oscillating cup, it is necessary to guarantee that the cup is at least 99 % filled with the liquid to make the meniscus effect negligible, while in the oscillating sphere, a large correction for the effect of air damping has to be estimated. In the vibrating wire viscometer, it is normally the average radius of the wire that is obtained from known values of viscosity and density (the standard reference point for viscosity of water at 20 °C has been used for that purpose,[11] but toluene has also often been chosen).[12−14] In the torsionally oscillating quartz crystal, the quality factor of the oscillator under vacuum is calculated from other independent measurements of viscosity. In the surface light scattering spectroscopy, it is necessary to have information about the dynamic viscosity of the vapor phase under saturation conditions, still difficult in many cases. In the falling-ball viscometer, it is necessary to know the diameter and sphericity of the ball and the terminal velocity of the ball with great accuracy, a fact not always achieved. All these methods will qualify as primary methods, as soon as these actual experimental limitations are overcome.

Consequently, the data obtained with these state-of-the-art instruments have smaller uncertainties, when compared with data obtained using other secondary methods, namely, the capillary viscometer (in any of its versions) or the rolling-ball viscometer, whose calibration parameters do not possess a clear physical meaning. The accepted international standard for water at 20 °C, based on the work of Swindells et al. at NBS (now NIST) in the early fifties,[3] an ISO standard[4] that was measured with capillary viscometry, was defined by international agreement, a procedure followed in some metrological work when no primary methods of measurement are available.

Finally, we need to state that to obtain viscosity of a fluid using any of these methods density values are required. The uncertainty of these data reflects directly the uncertainty of viscosity.

2.1. Oscillating Body. The oscillating disk viscometer is at present the most accurate oscillating body (disk, cup, cylinder, and sphere) instrument, both for measurements in the gas and in the liquid phases. It is essential for the accuracy of the instrument that a perfect parallel alignment of the fixed plates and the disk, as well as their flatness, is achieved. Mostly because this is virtually impossible in practice, the edge effect of the disk/plates must be calibrated. However, this edge effect is very small and can be easily accounted for in very well-designed instruments. The most accurate measurements in the liquid state of this type of viscometers have in the transient, free-decay mode of operation of the instrument used water as the calibrating fluid. Uncertainties better than 1 % can be achieved.[15] For high temperatures, viscometers based on the oscillating cup and the oscillating sphere have proved to achieve uncertainties of the order of (3 to 4) %, except for water, where uncertainties better than 2 % have been claimed.[16] In addition to several details of the oscillating system that have to be rendered negligible during design, including large air damping in the oscillating sphere, the measurement of temperature, especially in the cup, is quite tricky, and the construction of the spheres is rather difficult, causing additional uncertainties, that have to be accounted for.

2.2. Vibrating Wire. The vibrating wire viscometer involves the distortion, by an external applied field, of a solid body, normally a wire, immersed in the fluid.[17] These distortions cause periodic oscillations, and in the transient, free-decay mode of operation of the instrument, the damping of the oscillations is determined by the viscosity (and density) of the fluid.[18−20] Vibrating wire instruments can also be driven in steady-state, forced mode of operation, where the characteristics of the resonance curve for the transverse oscillations of the wire are correspondingly determined by the viscosity (and density) of the fluid.[12,13,20−22]

Quasi-primary methods, such as vibrating-wire viscometers, require some type of calibration, to guarantee the highest level of accuracy. In the mentioned type of technique, the average wire radius of the vibrating-wire sensor is obtained from a single experiment with the sensor immersed in a fluid of known viscosity and density rather than measured directly.[12,13,21,22] It is expected that it will be possible to construct, in the near future, a vibrating-wire instrument that can be operated with high accuracy on the basis of a direct measurement of the wire radius of the sensor.

Notwithstanding this point, vibrating-wire viscometers have several advantages in relation to other types of instruments. In fact, vibrating-wire sensors possess a rigorous set of working equations, the parameters of which have an unambiguous physical meaning. Combined with the simple geometry of the sensor, these characteristics avoid the need to perform any calibration as a function of temperature and pressure. Furthermore, vibrating-wire instruments are not affected by surface or interfacial tension effects, as is the case with most capillary instruments. This point is of the utmost importance because the only accepted primary reference point for viscosity is water at 20 °C, which exhibits a surface tension which is about twice the value of most of the other economically relevant fluids, such as hydrocarbons.

Moreover, a vibrating-wire viscometer has recently been developed[11] that can be calibrated with water at 20 °C and subsequently used to measure fluids with a viscosity on the order of 100 times more viscous than water. The instrument was validated by performing measurements of certified reference materials, with viscosity up to about 135 mPa•s, with an uncertainty of 0.8 % with direct traceability to the water reference point for viscosity,[11] including the uncertainty of this primary reference point. The use of this type of viscometers for a CRM N350 (Cannon), with viscosities up to 1.581 Pa•s, has also been reported using thick wires (0.2 mm), with the uncertainty rising to 10 %, which is claimed to be acceptable for the desired application to petroleum reservoir liquids.[13]

One of the obvious advantages of this type of instrument is that it completely avoids the need of stepping-up calibration procedures, within its measurement range. In particular, this instrument may be of high value, regarding the proposal of reference standard fluids for viscosity, having shown to be able to cover, up to the moment, a range up to 2 orders of magnitude above the water reference point.

2.3. Torsionally Oscillating Quartz Crystal. This method has been applied by different authors to the measurement of the viscosity of liquids.[17] This viscometer is based on the excitation of a quartz crystal cut along the optical axis, with a radiofrequency signal at its surface that produces a microscopic torsional vibrating movement. When the crystal is immersed in a viscous medium, these vibrations will induce a viscous wave, rapidly attenuated by the medium. The viscous drag exerted by the fluid on the surface of the crystal changes its resistance and resonance frequency, from those in vacuum. From the measurements of the conductance and capacitance properties of the crystal near resonance, the product of viscosity and density of the fluid can be obtained. Its chief advantage over other viscometers is that it has no moving parts (the movement of the crystal and the fluid is submicroscopic), which makes its application to wide ranges of temperature and pressure attractive.[23] Santos and Nieto de Castro measured the viscosity of toluene (purity in excess of 99.99 %) with a torsionally oscillating quartz crystal, for temperatures between (298.15 and 373.15) K and pressures up to 200 MPa.[24] The uncertainty of the temperature and pressure measurements was, respectively, 10 mK and 0.4 MPa. The quality factor of the oscillator in vacuum was not measured directly but calculated from viscosity measurements on toluene by other authors, namely, Gonçalves et al.,[25] performed with an independent method. As the damping in vacuum is much smaller than in the fluid, this procedure did not contribute to the overall uncertainty of the measurements by more than 0.03 %. The uncertainty of the data was estimated to be 1 %. However, the requirement of independent viscosity data to enable the calculation of the quality factor of the oscillator in vacuum imposes a restriction to its use.

2.4. Surface Light Scattering Spectroscopy. Dynamic light scattering is a versatile technique for the determination of thermodynamic and transport properties of fluids. Surface light scattering (SLS) analyzes the dynamics of surface fluctuations present at the phase boundary of the fluid system under investigation at a given wave vector. These fluctuations can be understood as thermally excited capillary waves. At low viscosity and/or large interfacial tension, surface fluctuations show an oscillatory behavior, and both properties are determined simultaneously by SLS. At high viscosity and/or low interfacial tension, surface fluctuations are overdamped and do not propagate. In this case, analyzing the mean lifetime of surface fluctuations, at a first approximation SLS gives only access to the ratio of dynamic viscosity to interfacial tension. The SLS method is restricted to fluid systems in the two-phase region. In contrast to conventional viscometers, SLS allows the determination of viscosity and interfacial tension in macroscopic thermodynamic equilibrium.

This technique has been extensively applied by Fröba and Leipertz,[26,27] and it has been converted to a very low uncertainty method of measurement of viscosity. It is an absolute method, as no calibration procedure using a fluid of known viscosity is needed. However, it cannot yet be considered a primary method of measurement because it is still necessary, in addition to the density of the liquid phase, to have information about the density and viscosity of the vapor phase under saturation conditions, still difficult in many cases, namely, for low vapor pressure liquids. Results for different working fluids and reference fluids demonstrate the applicability of the SLS technique to a wide range of viscosities, from about 10 μPa•s to 10 Pa•s with typical uncertainties between (1 and 3) %. The contactless operation makes SLS ideally suited for the investigation of viscosity at high temperatures. The uncertainty of the most recent measurements with liquid toluene is 1 %. In their most recent work, applied to diisodecyl phthalate (DIDP),[27] the authors claim an uncertainty of 1.4 %. In this work, because the viscosity of this liquid is very high, the vapor properties are negligible compared with those of the liquid phase. However, the interfacial tension of the sample has to be known, in addition to the density, to obtain the viscosity. This is the situation verified when either the viscosity of the liquid is very high and/or the interfacial tension is low.[27]

2.5. Falling Body. Falling-body viscometers make use of the time of free fall of some object under the influence of gravity through the fluid of interest as a measure of the fluid viscosity. Most commonly, spheres and cylinders have been used. The extreme difficulty of manufacturing falling bodies of the proper density so that the terminal velocity meets the very rigorous limitations imposed by the working equation (being based on Stokes' law) of the method (Reynolds Number, $Re < 0.1$) is the main disadvantage. The problem is further complicated by the necessary requirements of chemical compatibility with the sample and suitability of mechanical characteristics for fabrication. The majority of the existing falling-body instruments uses the spherical shape, which can be manufactured to very stringent specifications in terms of both surface finish and out-of-roundness, but suffers from the fact of being almost impossible to detect rotations, oscillations, and other movements of the falling body superimposed on the translational movement accounted for by the working equation. Finally, the method suffers from the geometrical constraint: length and diameter of the fall-tube, alignment of the fall axis with the tube axis, and end effects. Those effects impose conditions on the size of both the fall-tube and the falling body, to which it is difficult to adhere, which creates regions of the viscosity domain where the implementation of the method is not feasible.[28] However, most of these effects can be accounted for by a soundly based theoretically approach, rather than just by empirical schemes. Brizard et al.[10] have attempted to overcome most of these problems by synchronizing the movement of a linear digital video camera with that of the falling ball. This procedure permits the visualization of the ball trajectory and permits one to follow the variation of the ball speed along the tube until it reaches the terminal velocity. The authors claim an uncertainty of around 0.2 % for the highest viscosities. This method requires the use of very low Reynolds number and is highly dependent on image processing and storage and, therefore, amenable to systematic uncertainties, not accounted for in their uncertainty budget. However, these viscometers have a number of advantages for operation at high pressures or as relative instruments for industrial applications.

2.6. Capillary Flow. Capillary viscometers are the most extensively used instruments for the measurement of viscosity, especially of the liquid phase. They have the advantages of simplicity of construction (mostly in glass) and operation. They are in regular use in many countries for standard measurements at atmospheric pressure and can be used for absolute and relative measurements. Utilization of capillaries for relative measurements in research and industrial applications needs to be calibrated by resort, directly or indirectly, to specially designed capillaries, commonly known as *master viscometers*. The working principle of capillary viscometers is based on the Hagen–Poiseuille equation of fluid dynamics, but several corrections have to be made to the original equation, to accommodate their practical realization. Only *master capillary viscometers*, the so-called reference viscometers of ISO 3105[29] with fluid heads greater than 400 mm, adequately minimize nonideal contributions as end effects, geometrical effects, kinematic acceleration, surface tension, viscous dissipation, etc. However, their utilization involves some experimental difficulties, such as the requirement of special thermostatic baths, with constant temperature control for large depths.

The correction of the influence of surface tension on the dynamics of fluid flow in practical capillary viscometers (those built according to ISO 3105 defined types that must fit in a circular hole of 51 mm in diameter and be able to function in a bath 28 cm deep, with capillary lengths of roughly 10 cm) seems to remain a controversial subject and, in general, is not amenable to a completely rigorous solution.[30,31] Because many important fluids have a viscosity which is 10 orders of magnitude higher than the viscosity of water at 20 °C, its measurement, with calibrated capillary instruments, requires the step-up transfer of the calibration with water, using a significant number of different viscometers, with overlapping viscosity ranges. This step-up procedure, naturally, is a source of uncertainty and expense for the end-users. Brizard et al.[10] have shown that this step-up procedure transforms a relative uncertainty of 0.1 % obtained with water as the starting point into an uncertainty 50 times larger for a viscosity of 10 Pa·s. This will build up an uncertainty greater than 2 % for DIDP, which has a viscosity of 123.5 mPa·s at 20 °C. In their analysis, the uncertainty introduced by the step-up procedure is by far larger than was admitted before but possibly more realistic.[5]

Not considering the capillary flow method as primary, especially with the approach developed by Swindells et al.,[3] might be surprising, as values of the only existing standard measured by these authors are used in some of the quasi-primary methods described to calibrate some quantities, impossible to obtain with great accuracy. However, those authors did not use only one capillary but a set of specially designed glass capillaries, each one designed to minimize and extrapolate the effects mentioned above. It seems clear that the utilization of the methodology used by Swindells et al.[3] is, at present, nearly impossible. The costs involved in constructing and operating a structure that could perform the kind of viscosity measurements carried out by those authors would certainly be immense and possibly incompatible with current demands for productivity, even at a metrological institute level. Because of these problems, capillary viscometry, although very popular in metrological institutes, in practice should be considered as a secondary technique, of relative type.

3. Reference Liquids

Since the recommendations of Künzel et al.[5] in 1987 on reference materials for viscosity, more than two decades of research and development contributed to clarify many of the previous statements about the type of liquids to be used in calibrating laboratories, as well as on quality instrumentation. From the discussion presented above on the methods of measurement of viscosity, for low to moderate temperatures, it becomes apparent that calibrating liquids are necessary, for a wide range of viscosities, which can be employed directly by the end users, namely, industry, as standard reference materials to calibrate their working viscometers. As a necessary requirement, they must be very well characterized (by the manufacturer or "in house") and obtainable with high purity, as it well-known that viscosity is one of the physicochemical properties most affected by the presence of impurities.

In the next section, we discuss the possible liquids that can be used, with special emphasis on water alternative materials, such as toluene, aliphatic hydrocarbons, and alkyl esters. Their widespread use as reference fluids for viscosity will have, however, to be validated internationally. As a consequence, the actual CRM's produced by metrological institutes, or certified companies, with viscosity determined by step-up procedures from the viscosity of water at 20 °C will continue to play an important role for industry within the next years, namely, for high viscosities, but will not be discussed in this paper. It should be pointed out, however, that consulting the reference material certificate, issued by each producer, also regarding matters like the time limits for the validity of the certified values, is of the utmost importance.

The use of molten salts for high-temperature measurements, like $NaNO_3$, is also not discussed in the present paper but can be consulted in the work of Nunes et al.[32]

3.1. Water. Why? Water was the substance first chosen as the standard reference material for the measurement of viscosity because it fully satisfies all of the recommended requisites in terms of availability, purity, and safety of use. Nevertheless, because of its chemical characteristics, water is not sold as a standard reference material for viscosity, and its samples must, in general, be provided by the user, who must also assess the corresponding purity and purify it when necessary (usually by double distillation, deionization, and saturation with air).[5] Swindells et al.[3] used double distilled and air saturated water, while present day standards refer to type I water.[2] Therefore, its utilization is certainly more demanding in laboratory requirements and more time-consuming than the use of commercially available certified reference materials, even though these are just secondary standards. This will, in principle, also apply to other fluids, eventually accepted as standards, commercially available in the required state of purity, requiring very simple or no additional treatment.

Some special characteristics of water that make it such an important fluid also may create some particular difficulties, such as uncommonly high values of properties like surface tension, heat capacity, and thermal conductivity. Another problem with the use of water is the extension of the liquid range: because of the specific behavior at the liquid to solid transition (the expansion on freezing), most viscometers are unsafe to operate with water at temperatures near the lower end of the liquid range, shortening the range of recommended values for viscosity, namely, (15, 20, 23, 25, 30, and 40) °C, at 0.1 MPa.[4]

Due to the relatively low electrical resistivity of water, even after purification with standard laboratory equipment, its use may pose problems to the operation of some viscometers, e.g., by creating electrically conductive paths that might degrade the performance of the instruments. Moreover, its chemical characteristics may prove to cause problems due to reaction with some parts of the instruments.

3.2. Alternative Materials. Toluene and several other hydrocarbons also comply with the requisites for the use as standard reference materials. In fact, some of those substances are already being used as standard reference materials for other thermophysical properties like thermal conductivity and heat capacity.

3.2.1. Toluene. Toluene is in the liquid state under its saturation pressure over a very wide range of temperatures (from $T_{tr} = 178.15$ K to $T_{cr} = 593.95$ K, the normal boiling point temperature being $T_{nbp} = 383.764$ K)[33] and is, therefore, a desirable calibrating reference material for many properties as it can be obtained with a high purity. Recently, standard reference data for the viscosity of toluene between (210 and 400) K have been proposed (data refer to saturation line, so the pressure is not constant, but deviations from values at 0.1 MPa will be smaller than the uncertainty of the proposed reference data), as well as recommended values at 298.15 K and at other temperatures in this range.[34] Over this range, the viscosity varies by a factor of 5. This work has been performed under the auspices of the International Association for Transport Properties (IATP - http://transp.eng.auth.gr/) formerly the Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics.

The data available were categorized as primary and secondary data. Because no absolute measurements are available, only the data traceable to the water value at 20 °C of Swindells et al.,[3] corrected for ITS 90, were selected as primary data. The criteria chosen, according to the requirements of IUPAC[35] were:

1. Viscometer calibrated with water which had been distilled at least once.
2. Water viscosity data from Swindells et al.[3] used for calibration with variation with temperature given by the ISO standards, or any other source, provided that the values used are known, so that corrections can be applied.
3. A statement of uncertainty was made by the author or can be inferred.
4. The sample purity is stated.
5. The data dispersion when fitted to the polynomial equation, eq 1, is smaller than the uncertainty.
6. The descriptions of the measuring method and the experimental conditions are unambiguous.

The quality of the available experimental data imposed a limiting uncertainty for the primary data of 1 %, except for the temperature extremes where some points with an estimated uncertainty of (2 to 3) % were used. The purity of the samples used by the different authors was assessed and stated. In all cases, the purity of the samples exceeded 99.5 % for nonpurified samples and is better than 99.9 % for purified and dried samples.

An equation was developed for the viscosity of toluene, based on the IAPS formulation for the transport properties of water as developed by Sengers et al.[36] and Kestin et al.[37] The result obtained was[34]

$$\ln(\eta^*) = -5.2203 + \frac{8.964}{T^*} - \frac{5.834}{(T^*)^2} + \frac{2.089}{(T^*)^3} \tag{1}$$

where η^* and T^* are the dimensionless variables defined as

$$T^* = \frac{T}{298.15\ \mathrm{K}} \tag{2}$$

$$\eta^* = \frac{\eta(T)}{\eta(298.15\ \mathrm{K})}$$

and $\eta(298.15\ \mathrm{K}) = (554.2 \pm 3.3)\ \mu\mathrm{Pa \cdot s}$ is the standard value for the viscosity of toluene at 298.15 K and 0.1 MPa. This equation, capable of describing most of the experimental data sets within their own stated accuracy, for temperatures from (210 to 400) K, was established with 9 data sets composed of 83 data points and 4 different measurement techniques (capillary flow, oscillating disk, vibrating wire, and surface light scattering). The absolute uncertainty of the data calculated directly from this fit, using ISO definition ($k = 2$), is 6.9 μPa·s. Figure 1 shows the data selected plotted as a function of temperature. Data references can be found in the original paper.[34]

The reference correlation and the reference data proposed form an excellent basis of support, for a wide range of temperatures, of toluene as a reference fluid. In addition to this correlation, there was an effort to develop a wide range surface η (P, T) that includes data from (213 to 373) K and pressures to 250 MPa,[38] which extends the applicability of the fluid as a reference and the range of viscosity.

3.2.2. Nonane, Undecane, and Hexadecane. A number of hydrocarbons which are available with high purity possess good general characteristics to be a reference fluid, as an alternative

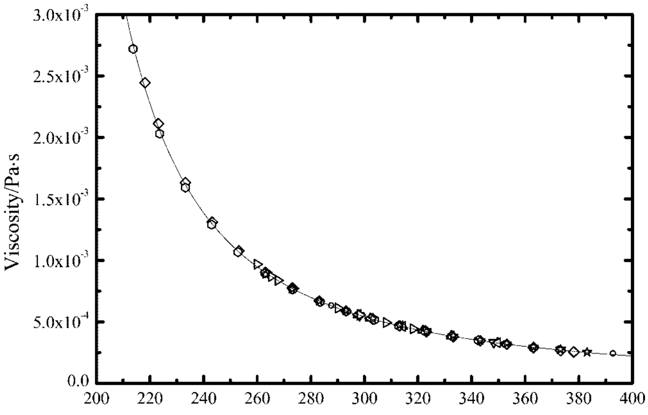

Figure 1. Primary data for the viscosity of toluene along the saturation line, for 213 K < T < 393 K. The line represents the proposed reference correlation (eq 1). Details of the primary data references can be found in the original paper.[34] Adapted with permission from ACS. □, Bauer 1984; ○, Dymond 1985; Δ, Gonçalves 1987; ∇, Dymond 1991; ◇, Kaiser 1991; triangle pointing left, Krall 1992; triangle pointing right, Dymond 1996; □, Assael 2000; ☆, Froba 2003.

to water. In particular, nonane, decane, and undecane, which have a viscosity near that of water at room temperature, have a large liquid stability range, low water solubility, and low vapor pressure.[5,39] They are aliphatic hydrocarbons, which do not react with most of the materials normally used in viscometer cells, filling lines, and manufacturing units and have low surface tension, heat capacity, and thermal conductivity values. Higher aliphatic hydrocarbons, like tetradecane and hexadecane, can also play a significant role, as their viscosity near room temperature is much higher than that of water or toluene, and at the boiling point of water, the viscosity of hexadecane is similar to that of water at room temperature.

3.2.3. Dialkyl Esters. The physical properties of dialkyl esters, like dialkyl phatalates, depend on the alkyl chains, so that, in principle, it should be possible to obtain a substance with a viscosity near a certain predefined value, by appropriate choice of the alkyl groups. Some characteristics, which are in general required for a suitable candidate to a reference fluid, may be found among this type of compounds, namely, a large liquid stability range, low water solubility, and low vapor pressure. Some difficulties arise however regarding the purity obtainable for these compounds. Several liquid alkyl esters, available commercially, have at room temperature a viscosity between the water reference point and approximately 200 mPa·s. This is very convenient because the existence of industrial reference liquids of moderately high viscosity would avoid the build-up of experimental uncertainty and costs incurred by step-up calibration procedures.[40] Viscosity results obtained with one alkyl ester, namely, diisodecyl phthalate (DIDP), have been published recently.[14,26,27,40−44] Caetano et al.[14] analyzed the existing viscosity, density, and surface tension data of DIDP at atmospheric pressure and proposed this liquid to be an industrial reference fluid for viscosity, with reference values for the viscosity of DIDP at three different temperatures and interpolation equations for the calculation of viscosity, density, and surface tension of this fluid at intermediate temperatures. Table 1 shows the proposed reference values for viscosity,[14] with an uncertainty of 1 %.

Table 1. Reference Values for the Viscosity of DIDP Proposed by Caetano et al.[14] with 1 % Uncertainty

T/K	η/mPa·s
293.15	123.5
298.15	88.5
303.15	65.0

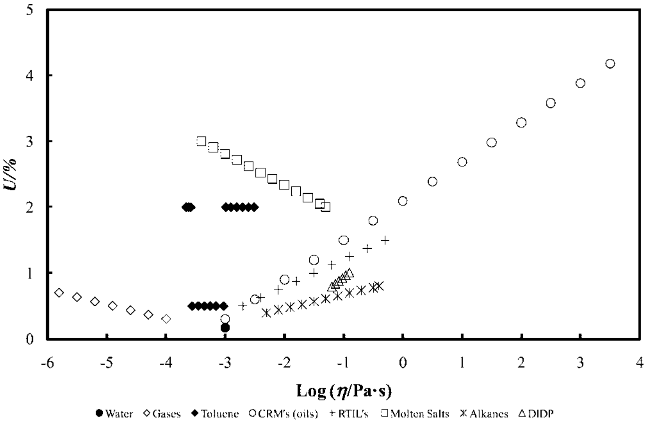

Figure 2. Viscosity ranges for different materials. ●, water; ◇, gases; ◆, toluene; ○, CRMs (oils); +, RTILs; □, molten salts; ∗, alkanes; Δ, DIDP. Water, toluene, alkanes, DIDP, and CRMs (Oils) are considered reference materials, certified or not. Values of the viscosity ranges of molten salts and RTILs are also shown, for comparison. Sketch of the uncertainty, U, that is possible to achieve with the best quality measurements is also displayed.

3.3. The Future. It is clear that the measurement of viscosity with high accuracy is approaching its state of maturity, whereby there are methods of measurement very close to being considered primary methods, reference fluids in some ranges of viscosity with standard reference data proposed, and a traceability chain to SI that can be applied. New applications are challenging scientists and industrialists, such as the immense variety of ionic liquids and the range of viscosity they cover.

Figure 2 displays the availability of calibrating liquids, for the different ranges of the viscosity scale (excluding non-Newtonian fluids), some of them not yet used in common calibration procedures for relative viscometers.[45] The ranges for the viscosity of low-temperature ionic liquids (LTILs) and high-temperature ionic liquids (HTILs, molten salts) are also displayed, and it can be seen that they fall in a range where toluene (already accepted as a certified reference material),[34] alkanes, and alkyl esters, including diisodecyl phthalate,[14] which are being suggested as international standards, are included. Figure 2 also shows a sketch of the uncertainties that can be achieved in the different viscosity zones with the best quality measurements. For ionic liquids, several problems arise, namely because they can either react with water or dissolve in it (whether it be merely from the atmosphere or present in any equipment lines), affecting the viscosity by a great amount.[46] This poses some additional problems in the handling of these compounds in the viscometers and emphasizes the need for water quantification before and after the measurements. From an analysis of the applicability of all the methods described in this paper to the measurement of the viscosity of ionic liquids (LTILs),[46] we can recommend the use of quasi-primary instruments, as the oscillating body (disk, cup, cylinder, and sphere), the torsionally oscillating quartz, and the vibrating wire for high-quality work, surface light scattering spectroscopy methods for specialized work, namely at high temperatures, and previously calibrated capillary flow viscometers for current laboratory work. In this latter case, the users must be aware of all the problems already mentioned about calibrating liquids and traceability chain to SI.

4. Conclusions

The importance of viscosity in the scientific and industrial world requires the existence of primary instruments, capable of producing high accuracy data on selected reference fluids, chosen to cover a wide range of viscosity values. However, although we are close to reaching this level, by solving the experimental and theoretical problems that still impede the "quasi-primary" methods, to be considered primary there is still a long way to go. The traceability to SI can therefore be attained in the *interim* by selecting a set of reference liquids, whose viscosity has been determined in different laboratories and by different quasi-primary techniques, whenever possible, covering wide ranges of viscosity. The metrological value of such an approach is higher than the current route only based on the value of the viscosity of water at 0.1 MPa and 20 °C and the stepping-up procedure. Such a procedure, once fully implemented, can avoid the higher uncertainties of the calibrations for high viscosity fluids and the chemical limitations of pure water, previously discussed.

Toluene and *n*-alkanes are, in our opinion, serious candidates for reference fluids, and one may expect them to have a very important role in the field of viscosity measurements in the next years. For moderately high viscosities, also DIDP should be considered for industrial reference fluid, if highly pure samples are available. However, as for ionic liquids, purity poses some constraints. The influence of the purity of commercial grades of this compound has been discussed in ref 14. Comparison of two samples of the same high purity (greater than 99.8 % by GC) suggested that the difference in viscosity was not greater than the experimental uncertainty of the method used (less than 1 %).

More than 50 years have passed since the reference book by Robinson and Stokes[1] appeared. Industrial metrology is actually based on calibration with commercial oils, but this procedure, although useful, cannot be considered the best. We can state that these 50 years have completely revolutionized the measurement of viscosity of liquids, not only in the quality of measured data but also in the diversity of excellent methods of measurement. It is perhaps now the time to widen the views to new scientific achievements, accepting that other instruments for measuring viscosity exist besides the omnipresent capillary method and in some instances superseding it.

It is also of the utmost importance to note that at present there seems to exist a lack of internationally accepted reference viscosity data as a function of pressure. The publication of the work by Assael et al.[47] under the auspices of the now extinct Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics, presently IATP, is one of the few attempts to fill this gap, which evidence a surprising indifference in the past for what is possibly a matter of great importance, as suggested, for example by several recent works by Harris and Bair,[42] Al Motari et al.,[43] Kandil et al.,[48] and Lundstrom et al.[49]

Thus, in conclusion, we have learned quite a lot, but not enough. Efforts must still be continued to make the entire field coherent and appropriate to deal with modern demands from diverse industries.

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