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# Viscosity Measurements of the Ionic Liquid Trihexyl(tetradecyl)phosphonium Dicyanamide $[P_{6,6,6,14}][dca]$ Using the Vibrating Wire Technique

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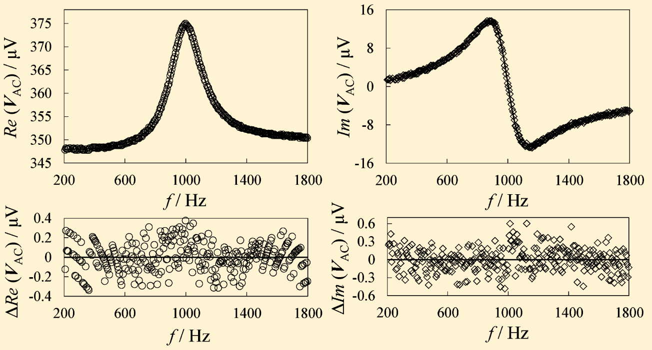
Ⓢ *Supporting Information*

**ABSTRACT:** The paper reports measurements of the viscosity of the ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide ($[P_{6,6,6,14}][dca]$) by means of a vibrating wire viscometer; the measurements have been carried out to demonstrate the applicability of the method to studies on electrically conducting liquids. To the knowledge of the authors, the present work reports only the second measurements of the viscosity of ionic liquids, using the vibrating wire method, ever published in the literature. The measurements were carried out at near ambient temperature at atmospheric pressure so that they can be compared with measurements made on the same sample using measurement techniques of previously proven validity. For this purpose measurements have also been carried out with two Ubbelohde capillary viscometers. Density measurements were undertaken using a U-tube Anton Paar density meter. All of the viscosity results reported here are mutually consistent within the estimated uncertainty of ± 2 % of the vibrating wire measurements, which confirms the applicability of the vibrating wire technique. However, the other viscosity literature data for of the same liquid deviate from the present results by more than the mutual estimated uncertainties of the measurements which may arise mainly from the different purities of the two samples.



## ■ INTRODUCTION

Ionic liquids continue to attract the attention of numerous researchers,[1,2] partly because they are plausible candidates to replace conventional solvents in many industrial processes; they are often referred to as "green solvents", owing to their low volatility and high potential for recycling. One very appealing characteristic of ionic liquids is that they can be synthesized according to the particular requirements of a specific process, adjusting their physical properties by changing the structure of the ions.[3,4] In particular, an appropriate selection of both the anion and the cation in the molecule enables the tailoring of an ionic liquid to yield the required thermophysical characteristics, for example, the desired viscosity range in a given range of temperature.[3,5]

In part because of the ability to tailor the properties of ionic liquids there have been an increasing number of studies of the thermophysical properties of ionic liquids aiming to find ionic liquids that can serve as new reference materials.[1,5] For example, the International Union of Pure and Applied Chemistry (IUPAC) has launched a project (Project 2002-005-1-100: Thermodynamics of ionic liquids, ionic liquid mixtures, and the development to standardized systems) which aims to study and propose the ionic liquid $[C_6mim][NTf_2]$ as a reference for several thermophysical properties.[1,2] In the present context, several ionic liquids would be appropriate to fill the viscosity gap of secondary, industrial reference fluids for viscosity from cyclopentane[6] ($\eta$ = 0.4 mPa·s, at $T$ = 298.15 K

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and $p$ = 0.1 MPa) and toluene[7,8] ($\eta$ = 0.77 mPa·s at $T$ = 293.15 K and $p$ = 0.1 MPa) to diisodecylphthalate (DIDP)[9] ($\eta$ = 123.5 mPa·s at $T$ = 293.15 K and $p$ = 0.1 MPa) and for higher viscosities. However, this aim has to some extent been frustrated because some impurities at very low levels in ionic liquids can have a major effect upon the viscosity of the liquid. Specifically, ions such as $Cl^-$ and $Br^-$, organic solvents, as well as traces of water, can strongly influence several thermophysical properties, which requires special care in handling ionic liquids.[10] We note the need to report the manner in which samples have been treated at all stages. In particular, avoiding the contact of the samples with humid air is of great importance, and the determination of the water contamination, before and after all property measurements, is crucial, since this may lead to important disagreements between the published results.[1,2] Thus, the pursuit of an ionic liquid as a standard reference fluid for viscosity has not yet been completely successful.

In these circumstances it is perhaps not surprising that large discrepancies have been reported between the results of measurements of the viscosity of each ionic liquids reported by different workers using different experimental techniques. Even at room temperature differences of up to the order of 120 % between different sources of results for the same ionic liquids have been reported.[5]

In attempt specifically to establish standard reference data for viscosity, deviations can still amount to 20 %, according to Nieto de Castro.[5] de Castro et al.[11] have recommended the use of quasi-primary instruments, for which exact working equations with a suitable set of corrections and a well-understood calibration are available for high quality work. One such technique, as mentioned by de Castro et al.,[11] is the vibrating wire technique. However, there exists only one publication on the viscosity of an ionic liquid determined with a vibrating wire viscometer.[12] Given that ionic liquids have a nonzero electrical conductivity, the conventional vibrating wire method could suffer from an additional problem because it uses electrical measurements in a bare metallic wire immersed in the fluid. Thus the technique needs validation before routine application to ionic liquids either empirically or by means of a completely new theoretical analysis of the technique. In the earlier work the results obtained were part of a program of measurements made by several authors using independent techniques in different laboratories, using samples of the same origin, but with, inevitably, different sample handling and therefore different levels of impurity, in particular of water contamination. The comparison among the techniques showed agreement within ± 5 %, and this was accepted as a validation of the vibrating wire technique for ionic liquids.[12] The level of uncertainty in this validation is rather greater than the precision of the measurements possible with the vibrating-wire viscometer. In the present paper we seek to improve upon this initial validation by employing different experimental techniques in our own laboratory and taking great care in the sample handling and in reporting the purity of the sample, in particular, monitoring the water contamination before and after all of the property measurements.

Thus, we present viscosity measurements of the ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide $[P_{6,6,6,14}][dca]$, using the vibrating wire technique and compare them with measurements made with other techniques of high accuracy, at atmospheric pressure. We therefore seek to validate the vibrating wire technique for modestly conducting ionic liquids. It is worthy of note that serendipitously the maximum viscosity tackled in this work significantly increases the upper limit of viscosity for measurements performed in our laboratory,[13] with this experimental method.

**Vibrating Wire Technique: Working Equations for the Forced Mode of Operation.** Vibrating wire viscometers consist of an axially tensioned, vertical metallic wire subject to a permanent magnetic field, perpendicular to its axis. The wire is immersed in a test fluid, the viscosity of which is to be measured. The vibrating wire technique involves the displacement of the wire from its rest position by means of the Lorentz force originated by passing an electric current through the wire under a magnetic field. In turn, this motion induces an electromotive force at the wire ends, which is directly related to the wire's velocity of oscillation through Faraday's law. The instruments can either be operated in the forced (steady-state) or the free-decay (transient) modes of operation.[14]

In the transient mode the wire oscillation is left to decay freely. In the steady-state mode, the signal that drives the wire into motion is an alternate current that spans a range of frequencies, encompassing the resonance frequency of the wire for its transverse oscillations, to obtain the corresponding resonance curve of the sensor. Comparisons of these different modes of operation, based on the results obtained with the same sensor, are described in the literature.[15,16]

The simplicity of the geometry of the vibrating element has enabled the development of a rigorous theoretical description, both of the mechanics of the oscillation of the wire and of the motion of the surrounding fluid. This theoretical description was developed by Retsina et al. both for the forced[17] and for the free decay[18] modes of operation. From the description of the former mode, the equation relating the velocity of the oscillations as a function of the frequency of the driving voltage is easily obtained.[19,20] Assuming that the resonance curve is obtained with constant driving current and that the magnetic flux is uniform, the complex voltage measured at the wire ends, as a consequence of the wire motion, is given, as a function of the frequency, $\omega$, by

$$\boldsymbol{V}_H = \frac{Y}{\omega(\beta' + 2\Delta_0) + i\omega(1 + \boldsymbol{\beta}) + \dfrac{\omega_0^2}{i\omega}} \tag{1}$$

where $Y$ is a constant dependent on the current intensity, the magnetic flux, and the mass per unit length of the wire; $\omega_0$ is the wire resonance frequency in the total absence of damping; $\Delta_0$ is the internal damping of the wire; $\beta'$ accounts for the viscous damping due to the fluid; and $\beta$ is the added mass due to the acceleration of the fluid (complex quantities are printed in boldface). The viscosity, $\eta$, and the density, $\rho$, of the fluid are related to $\beta$ and $\beta'$ through relations published by Retsina et al.[17]

The complex voltage drop measured at the wire ends, $\boldsymbol{V}_{AC}$, must be a result of the ohmic resistance of the wire, as well as inductive and capacitive effects arising from the circuitry utilized for the measurements. These distributed effects can be modeled by a lumped circuit, as shown in Figure 1, in series with the equivalent impedance, $\boldsymbol{Z}_H = \boldsymbol{V}_H/\boldsymbol{I}$, which arises from the motion of the wire, according to its hydrodynamic model (eq 1), where $\boldsymbol{I}$ is the current passing in the circuit.

Therefore, the resulting response, $\boldsymbol{V}_{AC}$, is the sum of two complex voltages

$$\boldsymbol{V}_{AC} = \boldsymbol{V}_{AB} + \boldsymbol{V}_H \tag{2}$$

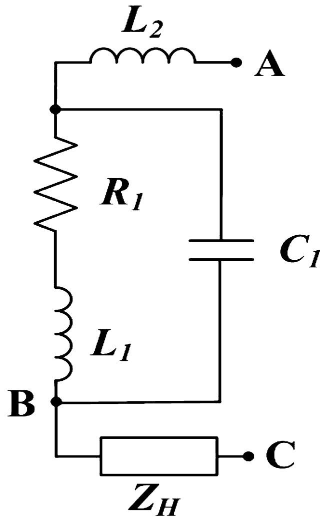

**Figure 1.** Equivalent circuit for a vibrating wire sensor.

Furthermore, the observed response signal of the sensor will be subject to background noise, bkg, which, according to Mehl,[21] is of the form

$$\text{bkg} = a + bi + f(c + di) \tag{3}$$

where $a$, $b$, $c$, and $d$ are real constants, and $f = (\omega/2\pi)$ is the frequency. The background noise should therefore be added to the model voltage of eq 2 above. However, the small quantity $a$ may be adequately incorporated in the ohmic resistance $R_1$ of the lumped circuit, while the frequency-dependent noise may be taken into account by the frequency dependent terms determining $V_{AB}$, so that the overall frequency response of the sensor may be described by

$$V_{AC} = I\left(i\omega L_2 + \left[\frac{1}{R_1 + i\omega L_1} + i\omega C_1\right]^{-1}\right) + bi + \frac{Y}{\omega(\beta' + 2\Delta_0) + i\omega(1 + \beta) + \frac{\omega_0^2}{i\omega}} \tag{4}$$

This model of the measured voltage at the wire ends aims to accommodate all of the distorting perturbations to which the measured frequency response is subject which may affect the value ascribed to the viscosity of the liquid sample after analysis of the experiment.

Following the measurement of the resonance curve of the driven vibrating wire system, the viscosity is determined essentially by fitting eq 4 to it. In this process it is usual to determine certain of the instrument constants by independent means. So, for example, the wire radius may be determined by calibration with a fluid of known viscosity[13,19] or measured directly[22] as may the density of the wire material. The internal damping of the wire can be determined independently from measurements of the frequency response of the sensor under vacuum.[19] Equally, the density of the test fluid can be determined independently from literature sources or from a special measurement, and the current through the wire, $I$, can be measured directly in each run. The remaining parameters of eq 4 ($R_1$, $L_1$, $L_2$, $C_1$, $b$, and $Y$) together with the undamped resonance frequency, $\omega_0$, and the viscosity are then determined from the fit to the resonance curve. In our work the fitting of experimental data was accomplished using MatLab software FMINSEARCH (multidimensional nonlinear minimization with a Nelder−Mead algorithm). The objective function to be minimized is identical to the one used by Mehl:[21]

$$\chi^2 = \sum_{i=1}^{N} |V_{\exp,i} - V_{\text{calc},i}|^2 \tag{5}$$

where susbcripts exp,$i$ and calc,$i$ refer to the $i$th experimental and calculated complex voltages, respectively.

Typical in-phase and quadrature responses are shown in Figure 2. These curves have been obtained with a sample of $[P_{6,6,6,14}][\text{dca}]$ at 298.20 K.

The adequacy of the model circuit in series with the hydrodynamic impedance in Figure 1 has to be verified in practice. Several tests are described in the Experimental Section.

## ■ EXPERIMENTAL SECTION

This section is devoted to several aspects of the experimental techniques employed to ensure the quality of the experimental results subsequently presented. We begin with a description of the handling of the test materials which have been common to all of the experiments, as well as the sources of the fixed parameters of the experimental cell. This is followed by a description of the means of validating the working eq 4 for the vibrating-wire viscometer employed for data reduction and the measurement of viscosity. Subsequently we describe briefly the two other viscometers used to provide comparative viscosity data for the same fluid sample as has been studied in the vibrating wire device.

**Materials.** The ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide ($[P_{6,6,6,14}][\text{dca}]$) was prepared (see Supporting Information for details) following a recommended procedure[23] using trihexyl(tetradecyl)phosphonium chloride $[P_{6,6,6,14}]\text{Cl}$ (100 g scale) generously provided by Cytec (Canada). All of the remaining reagents required for the reaction were purchased from Aldrich, Fluka, or Acros and used as received or after purified as prescribed. The purification was performed by washing with distilled water, followed by column chromatography (charcoal and silica) and solvent evaporation under vacuum (7 days, at approximately 0.1 kPa and 323 K) obtaining $[P_{6,6,6,14}][\text{dca}]$ as a pale yellow oil.

Nuclear magnetic resonance (NMR) spectra were measured on a BrukerAvance 400 Ultrashield spectrometer. All NMR spectra (see Supporting Information) were recorded in deuterochloroform, with reference to tetramethylsilane. The results are summarized in Table S1 in the Supporting Information which, particularly for the $^{13}$C NMR spectrum (see Figure S1 in Supporting Information), evidence the homogeneity of the sample.

An elementary analysis was carried out on a sample using a Leco, model Trunspec, with the following results (in mass fractions): C, 73.45 %; H, 12.82 %; N, 7.68 %; which can be compared to the calculated data for $C_{34}H_{68}N_3P$: C, 74.26 %; H,12.46 %; N, 7.64 %.

The chlorine content of our sample was measured at Laboratório de Análises (IST) by ion chromatography: guard column, AG4A Dionex; column, AS4A Dionex; the eluent was an aqueous solution of bicarbonate/carbonate (1.8 mmol·dm$^{-3}$/1.7 mmol·dm$^{-3}$), flow rate of 2 cm$^3$·min$^{-1}$, and the samples were

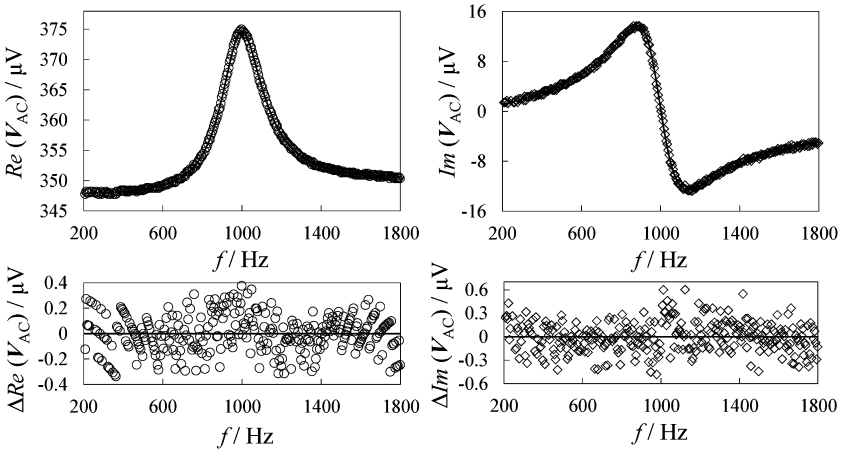

**Figure 2.** In-phase, Re($V_{AC}$), and quadrature, Im($V_{AC}$), experimental voltage curves obtained with a sample of $[P_{6,6,6,14}]$[dca] at 298.20 K and the corresponding fitting eq 4 (straight line). The deviations, ΔRe($V_{AC}$) and ΔRe($V_{AC}$), in the lower plots are the differences between the experimental points and those calculated by eq 4.

dissolved in acetonitrile (volume fraction of 10 %). The chlorine content obtained had a mass fraction of 0.02 %.

The samples were dried under vacuum for two days at about 60 °C and left under vacuum for several days at room temperature. The collection of samples for all of the various measurements described was made under vacuum or under helium atmosphere. The water content of the samples was monitored, before and after all of the property measurements we have made, using Karl–Fisher coulometric titration, with an 831 KF coulometer from Metrohm (Germany). There was no significant variation of the water content throughout the measurement and handling cycles of any sample.

**Density Measurements.** The working equations for the vibrating-wire viscometer make it clear that the density of the fluid is required to evaluate the viscosity. In this work we have chosen to measure the density of our sample using an automatic Anton Paar U-tube densimeter (model DMA 5000). The indicated repeatability of the temperature is 0.001 K. The overall uncertainty of the present density measurements is estimated to be less than ± 0.1 %. The densimeter was calibrated with air and water, using standard values.[24−26] The filling of the U-tube with the sample of $[P_{6,6,6,14}]$[dca] was carried out under nitrogen flow to avoid water contamination from atmospheric air and water vapor.

**Vibrating Wire Viscosity Measurements.** The measurements have been carried out with a vibrating-wire sensor that has been described previously by Caetano et al.[13,27] The vibrating wire sensor, comprising a tungsten wire subject to a magnetic field, created by permanent magnets placed externally, was mounted within a stainless steel vessel in a silicon oil thermostatic bath, with a recirculating immersion cooler. The bath was controlled by a Hart Scientific (USA) temperature controller, model 2100, with a platinum resistance thermometer as a sensor. The temperature of the thermostatic oil was maintained stable to within ± 0.003 K for over 30 min, measured with a 100 Ω-platinum resistance thermometer, measured with a digital multimeter (Prema, model 6001), with an overall estimated uncertainty of ± 0.05 K (based on a recent calibration by EIA, Lda, Portugal).

For the measurements, a lock-in amplifier (Perkin-Elmer, model PE7225) has been used both as a synthesizer of the variable-frequency driving current and as a voltmeter to measure the potential drop across the vibrating-wire sensor as described before.[13,27] A standard 100 Ω resistor (grade S standard resistor type 3504D from H. Tinsley & Co. Ltd., U.K.) was connected in series with the sensor. The electric current passing through the wire was determined by measuring the voltage drop across this resistor. A computer was used to command the instruments and to acquire the raw data, through a GPIB-USB-HS interface from National Instruments.

The instrument parameters for the current work are shown in Table 1. The wire radius has been determined by the calibration with water at 293.15 K and 0.1 MPa, the primary reference point for viscosity, using eq 4. The internal damping was obtained from the resonance curves under vacuum, as described before,[19,20] and the wire density was taken from the literature.[28]

**Table 1. Cell Parameters at 293.15 K**

| | | |
|---|---|---|
| radius of the wire | $R$ | 199.71 $\mu$m |
| internal damping | $\Delta_0$ | $1.3\cdot10^{-4}$ |
| wire density | $\rho_s$ | $19.23\cdot10^3$ kg·m$^{-3}$ |

The repeatability of the measurements is better than ± 0.3 %. A sensitivity analysis has been carried out, to estimate the uncertainty of the present results. As has been observed before,[13] the major single contribution to the uncertainty from the cell parameters arises from the wire radius. The remaining parameters contribute less and, in fact, are made negligible in practice, as a result of the calibration used to determine the wire radius. An estimate of the overall relative uncertainty of the present vibrating wire measurements yields ± 2 %, taking into account the comparison of results obtained by capillaries, carried out in the present work. Furthermore, it should be noted that the uncertainty value indicated takes into account an estimate of the effect of the uncertainty of the water contamination in our samples as measured by Karl Fischer titration. This was based on the water content after the viscosity measurements. The sensitivity of the viscosity of $[P_{6,6,6,14}]$[dca] to the water content was estimated using data obtained in the present work. The data used and the estimation procedure of that effect are described in a later section.

**Capillary Viscosity Measurements.** The independent supporting measurements of the viscosity of the same test samples were performed using a commercial automatic Schott

ViscoSystem AVS 440 measuring unit, fitted with an Ubbelohde viscometer, type 541 23/IIC, from Schott-Geräte. Measurements with a micro-Ubbelohde capillary, type 537 30/III, were also performed. The Ubbelohde capillary was calibrated[9] with a standard specimen 100B, from PTB, Germany. The micro-Ubbelohde capillary was manufactured and calibrated[29] by SI Analytics GmbH, Mainz, Germany. The calibration was made by comparison with reference viscometers, of which the constants were determined at PTB, Germany. The estimated overall uncertainty of the temperature readings was ± 0.05 K, and the temperature variation during each measurement was less than ± 0.01 K. Flow times were between (200 and 1000) s. Five sets of five measurements each were performed, having deviations from the mean smaller than ± 0.1 %.

All of the inlets used for air admission to the Ubbelohde and micro-Ubbelohde viscometers under routine operation were fed with nitrogen, through filters filled with calcium chloride and silica gel, to reduce water contamination during the special measurements needed here. Similarly, the outlets were provided with the same kind of filters.

In the present work it is important that we pay close attention to the uncertainty of the viscosity measurements with our two capillary viscometers because they serve as our standard for validation of the vibrating-wire viscometer. The uncertainty of the measurements performed with the Ubbelohde capillary receives its most important contribution from the calibration performed with the PTB 100B reference substance. The expanded uncertainty at a $2\sigma$ level is estimated to be less than 1.5 %. However, an estimate of the error associated with the difference of the surface tension of $[P_{6,6,6,14}][dca]$ and of the calibrating fluid substantially increases the overall uncertainty of those measurements. According to Bauer and Meerlender,[30] the effect of the surface tension difference and its correction depends directly on the difference of the ratio of the surface tension to the density, $\sigma/\rho$, between the sample and the calibrating fluid. Using the correlation eq 7 with parameters of Table 3 to calculate the density of $[P_{6,6,6,14}][dca]$, and its surface tension at 25 °C, measured by Kilaru et al.[31] (eq 4 of ref 33), the ratio $\sigma/\rho$ is $39.1\cdot10^{-6}$ $m^3\cdot s^2$. The same ratio for the liquid used to calibrate the Ubbelohde capillary utilized in the present measurements is[32] $\sigma/\rho$ = $35.2\cdot10^{-6}$ $m^3\cdot s^2$, at the same temperature. The surface tension effect was estimated as described in our previous work,[32] by means of eq 1 indicated in that reference. For that purpose the values of the ratio of the surface tension to the density, $\sigma/\rho$, and of the viscosity of the reference liquids PTB100B and Cannon S60 were taken from ref 32. An estimate of the limit of this systematic error yielded about −0.4 %. Therefore, the overall uncertainty of the measurements performed with the Ubbelohde capillary is estimated to be 1.6 %.

The uncertainty of the measurements carried out with the Ubbelohde microcapillary has its highest single contribution from the uncertainty of the calibration constant supplied by Schott Instruments. For these measurements, the uncertainty due to the surface tension effects was assumed to be of the same magnitude of the systematic error estimated for the Ubbelohde capillary. This estimate is based on the good agreement of the results obtained by the two instruments. An overall estimate of the uncertainty of the measurements of both capillaries used is of the same order of magnitude, namely, 1.6 %. It is to be noted that these uncertainties take into account an estimate of the effect of an uncertainty of the water content in our samples as measured by Karl Fischer titration.

**Tests of the Working Equation.** To check explicitly the effect of the nonzero electrical conductivity of our ionic liquid sample upon the overall resistance of the vibrating wire sensor, we have measured the voltage drop across the terminal posts (between which the wire is usually clamped), in the absence of the wire, as a function of the frequency of the driving signal, from about (40 to 2000) Hz. The results have shown that the electrical resistance caused by the liquid in the measurement cell is essentially constant in the interval of frequencies used for the viscosity measurements. The equivalent resistance arising from the presence of the conducting liquid in the cell is about 4 orders of magnitude higher than the resistance of the tungsten wire itself, and so its effect is essentially negligible in the present work.

According to eq 4, the baseline is given by eq 6 and relates to the description of the ohmic resistance of the wire, the effect of the stray capacitances and inductances in the circuit and to the background noise.

$$\boldsymbol{V}_{\mathrm{AB}} = \boldsymbol{I}\left(i\omega L_2 + \left[\frac{1}{R_1 + i\omega L_1} + i\omega C_1\right]^{-1}\right) + bi \qquad (6)$$

This baseline description was tested by measuring the in-phase and quadrature voltages at the wire ends, using the same current, ***I***, in a range of frequencies from (200 to 1800) Hz, having a sample of $[P_{6,6,6,14}][dca]$ at about 298 K, when (i) having the usual assembly or (ii) having the magnets removed from their usual place. The ohmic resistance of the wire, the stray capacitances, inductances, and noise should be approximately the same in both situations. A very good agreement of the direct measurement of the baseline as a function of frequency (i.e., without magnets) with the baseline given by eq 4 with the parameters obtained from the fitting of eq 6 to the frequency response (with magnets) has been verified. This comparison provides good support for eq 6 and by implication for eq 4 and their description of the experimental technique even for ionic liquids.

One further test of the ability of our working equations to describe the vibrating-wire sensor has been conducted, by introducing deliberately into the connection of the cell additional stray capacitances or inductances while keeping all other elements of the experiment identical, thus producing a modification of the background noise signal against which the small induced emf (approximately, 0.1 mV) across the ends of the wire must be discerned. In Figure S2 of the Supporting Information the in-phase and quadrature voltage signals, measured at the wire ends as a function of frequency, for two different runs, at the same temperature, are shown. Equation 4 yields identical values, within experimental uncertainties, for the physically meaningful parameters, such as the viscosity of the liquid, while those that represent the stray capacitances and noise will be altered. As expected, by fitting eq 4 to the experimental data, the parameters obtained, in particular the lumped inductance and capacitance elements of the model circuit differ from each other, and the other parameters remain essentially constant. It is of paramount importance that these parameters correspond to the quantities that are endowed with a clear physical meaning, namely, the viscosity, $\eta$, the undamped resonance frequency, $\omega_0$, and the ohmic resistance of the wire, $R_1$. It is noteworthy that the difference of viscosity obtained in the two experiments is less than 0.3 %, which is commensurate with the estimated repeatability of the measurements.

## RESULTS AND COMPARISONS

**Density.** The experimental results of the density measurements, from about (291 to 321) K, under atmospheric pressure are shown in Table 2. The water content of the sample was 44 mg·kg$^{-1}$ and 67 mg·kg$^{-1}$, before and after the measurements, respectively. The measurements were carried out at intervals of about 2.5 K. The Anton Paar DMA 5000, used for the measurements has a built-in system for automatically correcting the effects of the viscosity difference of the samples on the density results.

**Table 2. Density Measurements of [$P_{6,6,6,14}$][dca] as a Function of Temperature and at Atmospheric Pressure. First Two Columns: Data Obtained in Ascending Temperatures; Last Two Columns: Measurements Performed at Descending Temperatures. The Water Content of the Sample Was (44 and 67) mg·kg$^{-1}$ Before and After the Measurements, Respectively**

| $T$<br>K | $\rho$<br>kg·m$^{-3}$ | $T$<br>K | $\rho$<br>kg·m$^{-3}$ |
|---|---|---|---|
| 290.66 | 902.3 | 320.65 | 885.3 |
| 293.15 | 900.9 | 318.15 | 886.7 |
| 295.65 | 899.5 | 315.65 | 888.1 |
| 298.15 | 898.0 | 313.16 | 889.5 |
| 300.65 | 896.6 | 310.66 | 890.9 |
| 303.15 | 895.1 | 308.16 | 892.3 |
| 305.65 | 893.7 | 305.65 | 893.7 |
| 308.15 | 892.3 | 303.16 | 895.1 |
| 310.65 | 890.9 | 300.66 | 896.6 |
| 313.15 | 889.5 | 298.16 | 898.0 |
| 315.65 | 888.1 | 295.66 | 899.5 |
| 318.15 | 886.7 | 293.16 | 900.9 |
| 320.65 | 885.3 | 290.66 | 902.3 |

The density data in Table 2 were correlated with the temperature by an equation of the form

$$\rho(T) = l + mT + nT^2 \tag{7}$$

The corresponding fitting parameters, $l$, $m$, and $n$ are shown in Table 3, together with the statistical parameters, root-mean-square deviation, rmsd, and bias, defined, respectively, as

$$\text{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{Z_{\text{exp},i}}{Z_{\text{calc},i}} - 1\right)^2\right]^{1/2} \tag{8}$$

and

$$\text{bias} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{Z_{\text{exp},i}}{Z_{\text{calc},i}} - 1\right) \tag{9}$$

where $N$ is the number of experimental points, $Z_{\text{exp},i}$ is the $i$th experimental point of the property $Z$ (density or viscosity) and $Z_{\text{calc},i}$ is the corresponding value obtained by a fitting equation. Figure 3 shows a deviation plot of the results shown in Table 2 from the correlation eq 7, with the parameters of Table 3.

**Table 3. Parameters of Equation 7 for the Experimental Density Measurements Shown in Table 2 and the Corresponding rmsd and bias of the Density Data from the Fitting**

| | |
|---|---|
| $l$/kg·m$^{-3}$ | 1114.20 |
| $m$/kg·m$^{-3}$·K$^{-1}$ | −0.87307 |
| $n$/kg·m$^{-3}$·K$^{-2}$ | 4.961·10$^{-5}$ |
| rmsd | 1.1·10$^{-5}$ |

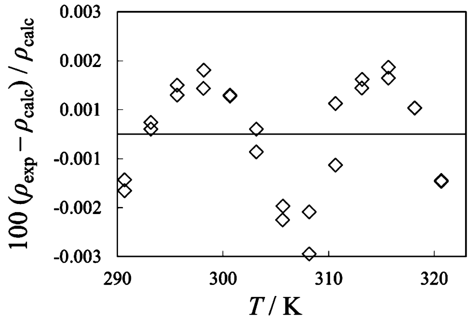

**Figure 3.** Deviation plot of the density results shown in Table 3 from the correlation eq 7, with the parameters given in Table 2.

The repeatability of the density results is better than ± 0.01 %, and the estimated overall uncertainty is expected not to exceed ± 0.1 %.

**Comparison of Density Results.** Two density data sets of [$P_{6,6,6,14}$][dca] have been found in the literature. Kilaru et al.[31] measured a sample from Cytec at temperatures of (298 to 333) K. The water content of the sample was reported to be 4230 mg·kg$^{-1}$, while the chlorides content was said to be 0.5 %; both are significantly different from our sample. The density was measured with a pycnometer. The temperature uncertainty was ± 0.1 K, and the standard deviation of the results is 0.5 kg·dm$^{-3}$. Pereiro et al.[33] also measured the density of a sample of [$P_{6,6,6,14}$][dca] from Cytec, in the range (278.15 to 343.15) K, with a chloride content of 205 mg·kg$^{-1}$, measured by potentiometry and reported a water content smaller than 125 mg·kg$^{-1}$, much nearer to the characteristics of our sample. The results of Kilaru et al.[31] deviate systematically from the present measurements by about +2.5 %. In Figure 4 the deviations of the data obtained by Pereiro et al.[33] from the correlation equation (eq 7) of the present results are shown. The data of Pereiro et al.[33] are systematically higher than the present results, but all of the deviations are within +0.1 %, from our fitting equation, which is commensurate with the estimated uncertainty of our measurements.

**Viscosity by the Vibrating Wire Technique.** The results of the viscosity of [$P_{6,6,6,14}$][dca] obtained with the vibrating wire technique are shown in Table 4.

The data from Table 4 were correlated as a function of temperature using the Vogel−Fulcher−Tammann (VFT) equation.[34]

$$\eta(T) = AT^{0.5}\exp\left(\frac{k}{T - T_0}\right) \tag{10}$$

where $A$, $k$, and $T_0$ are fitting parameters. It is noteworthy that this equation has recently been identified by several authors as especially useful to describe the viscosity of ionic liquids, as a function of temperature.[35,36] The fitting parameters of eq 10

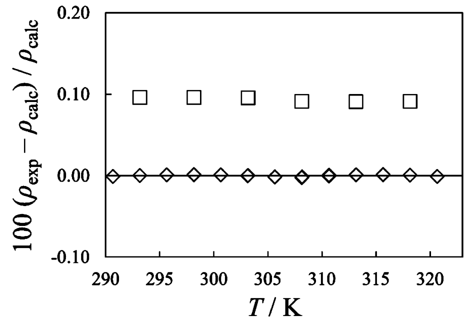

**Figure 4.** Deviations of the density results for $[P_{6,6,6,14}][dca]$, obtained by Pereiro et al.,[33] □, and in the present work, ◇, from the correlation of eq 7 with parameters from Table 3.

**Table 4. Vibrating Wire Viscosity Measurements. The Water Content of the Sample Was (53 and 300) mg·kg$^{-1}$, Before and After the Measurements, Respectively**

| $T$ | $\eta$ | $T$ | $\eta$ | $T$ | $\eta$ |
|---|---|---|---|---|---|
| K | mPa·s | K | mPa·s | K | mPa·s |
| 293.142 | 505.2 | 298.204 | 378.4 | 303.176 | 287.9 |
| 293.143 | 505.5 | 298.204 | 377.3 | 303.176 | 287.7 |
| 293.142 | 505.3 | 298.204 | 378.4 | 303.177 | 288.5 |
| 293.142 | 505.1 | 298.204 | 378.0 | 303.176 | 288.0 |
| 293.142 | 505.9 | 298.203 | 378.1 | 303.176 | 287.6 |
| 293.142 | 506.7 | 298.203 | 378.0 | 303.176 | 288.1 |
| 293.142 | 506.2 | 298.203 | 378.5 | 303.176 | 287.5 |
| 293.142 | 505.3 | 298.203 | 378.2 | 303.178 | 287.8 |
| 293.142 | 506.6 | 298.203 | 377.9 | 303.177 | 287.6 |
| 293.142 | 505.7 | 298.202 | 377.3 | 303.177 | 288.1 |
| 293.142 | 506.6 | 298.202 | 378.1 | 303.176 | 288.1 |
| 293.143 | 506.1 | 298.204 | 378.8 | 303.176 | 288.5 |
| 293.142 | 505.5 | 298.203 | 377.4 | 303.177 | 288.2 |
| 293.142 | 505.2 | 298.203 | 378.4 | 303.177 | 287.3 |
| 293.142 | 506.4 | 298.204 | 378.1 | 303.177 | 288.5 |
| 293.142 | 506.6 | 298.204 | 378.4 | 303.177 | 288.5 |
| 293.142 | 506.3 | 298.204 | 377.4 | 303.176 | 287.9 |
| 293.143 | 506.7 | 298.204 | 378.0 | 303.176 | 287.7 |
| 293.143 | 506.6 | 298.204 | 377.7 | 303.177 | 288.5 |
| 293.143 | 506.4 | 298.204 | 378.5 | 303.176 | 288.0 |
| 293.143 | 505.1 | | | | |
| 293.143 | 506.0 | | | | |
| 293.143 | 504.9 | | | | |
| 293.143 | 506.7 | | | | |
| 308.198 | 219.7 | 313.182 | 170.9 | 318.186 | 134.0 |
| 308.198 | 220.0 | 313.182 | 171.0 | 318.186 | 134.5 |
| 308.198 | 220.0 | 313.182 | 171.2 | 318.186 | 134.6 |
| 308.198 | 219.8 | 313.182 | 171.2 | 318.186 | 134.1 |
| 308.198 | 220.0 | 313.182 | 171.1 | 318.186 | 134.3 |
| 308.197 | 219.9 | 313.182 | 171.1 | 318.186 | 134.4 |
| 308.197 | 219.7 | 313.182 | 171.2 | 318.185 | 134.4 |
| 308.198 | 220.0 | 313.183 | 171.2 | 318.186 | 134.4 |
| 308.195 | 220.4 | 313.182 | 171.2 | 318.186 | 134.3 |
| 308.198 | 220.3 | 313.182 | 170.8 | 318.186 | 134.6 |
| 308.199 | 219.6 | 313.182 | 171.3 | 318.186 | 134.7 |
| 308.198 | 220.2 | 313.182 | 170.9 | 318.186 | 134.6 |
| 308.198 | 219.6 | 313.183 | 170.9 | 318.186 | 134.1 |
| 308.198 | 219.9 | | | 318.186 | 134.4 |
| 308.198 | 220.2 | | | 318.186 | 134.3 |
| 308.198 | 219.6 | | | 318.187 | 134.4 |
| 308.198 | 219.8 | | | 318.186 | 134.2 |

together with the rmsd and bias of the experimental points from the correlation equation are shown in Table 5. The deviations of the experimental viscosity values from the fitting equation are shown in Figure 5. All of the deviations are within ± 0.5 %.

**Table 5. Fitting Parameters of Equation 10 for the Experimental Viscosity Data Obtained by the Vibrating Wire Technique and the Corresponding Relative Root-Mean-Square Deviation, rmsd, and bias of the Data**

| | |
|---|---|
| $A$/mPa·s·K$^{-1/2}$ | 2.2624·10$^{-5}$ |
| $k$/K | 3276 |
| $T_0$/K | 60.46 |
| rmsd | 0.18 % |
| bias | 0.00 % |

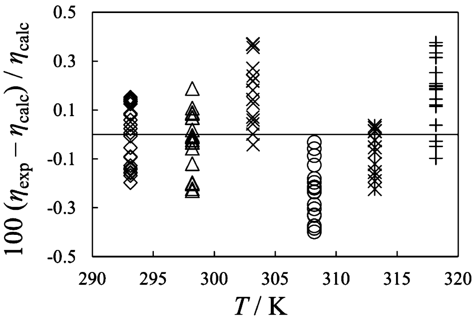

**Figure 5.** Deviations of the experimental viscosity results obtained with the vibrating wire method, for $[P_{6,6,6,14}][dca]$, shown in Table 4, from the fitting eq 10, with the parameters given in Table 5.

All of the data have been obtained in experimental runs wherein the temperature drift was smaller than 0.01 K. The fittings of eq 4 to the experimental complex voltage frequency responses have, typically, a complex deviation, CD, defined as

$$\mathrm{CD} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{|\boldsymbol{V}_{\mathrm{exp},i} - \boldsymbol{V}_{\mathrm{calc},i}|}{|\boldsymbol{V}_{\mathrm{calc},i}|}\right)^{2}\right]^{1/2} \tag{11}$$

of 0.05 %, where $\boldsymbol{V}_{\mathrm{exp},i}$ is the experimental $i$th point of the complex voltage, $\boldsymbol{V}_{\mathrm{calc},i}$ is the corresponding value obtained by eq 4, and $N$ is the number of points in a run.

The water content of the sample was (53 and 300) mg·kg$^{-1}$, before and after the measurements, respectively.

Subsequently, all of the viscosity data were assigned to nominal temperatures. The viscosities, $\eta(T_{\mathrm{nom}})$, at each nominal temperature, $T_{\mathrm{nom}}$, are shown in Table 6. For each nominal temperature, the viscosity $\eta(T_{\mathrm{nom}})$ is the mean value of, at least, 13 measurements that were performed at temperatures differing less than 0.01 K from $T_{\mathrm{nom}}$, and subsequently corrected to the nominal temperature by means of the equation

$$\eta(T_{\mathrm{nom}}) = \frac{\eta(T)T^{0.5}}{T^{0.5}\exp\left[\dfrac{k}{T - T_0} + \dfrac{k}{T_0 - T_{\mathrm{nom}}}\right]} \tag{12}$$

where, $\eta(T)$ is the experimental viscosity at temperature $T$ and $T_0$ and $k$ are fitting parameters of the VFT equation, eq 10, listed in Table 5. The last column of Table 6 lists the standard

**Table 6. Nominal Mean Values of the Viscosity, $\eta$, Measured with the Vibrating Wire Technique at Nominal Temperatures, $T_{\mathrm{nom}}$, and Atmospheric Pressure of $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$, Obtained with eq 12, with Parameters of Table 5**

| $T_{\mathrm{nom}}$ | $\rho^{a}$ | $\eta$ | $\sigma_{\mathrm{m}}{}^{a}$ |
|---|---|---|---|
| K | $\mathrm{kg \cdot m^{-3}}$ | mPa·s | mPa·s |
| 293.14 | 900.9 | 505.9 | 0.13 |
| 298.20 | 898.0 | 378.0 | 0.10 |
| 303.18 | 895.1 | 288.0 | 0.10 |
| 308.20 | 892.3 | 219.9 | 0.06 |
| 313.18 | 889.4 | 171.1 | 0.04 |
| 318.19 | 886.6 | 134.4 | 0.05 |

[a] $\sigma_{\mathrm{m}}$ is the standard deviation of the mean value, $\eta(T_{\mathrm{nom}})$; density values at nominal temperatures, $\rho(T_{\mathrm{nom}})$, were obtained from eq 7, with parameters from Table 3.

deviation of the mean values of $\eta(T_{\mathrm{nom}})$. For each temperature, the density, $\rho(T_{\mathrm{nom}})$, is given in the second column. These were calculated by the correlation eq 7, with parameters from Table 3.

The viscosity measurements at each nominal temperature were carried out with at least three different currents, from (7 to 15) mA. This is evidence that the viscosity results do not depend on the currents used, within the repeatability of the measurements, as required by the theoretical model underlying eq 1.

The standard deviation of the mean, $\sigma_{\mathrm{m}}$, shown in Table 5 is defined as

$$\sigma_{\mathrm{m}} = \left[ \frac{1}{N(N-1)} \sum_{i=1}^{N} (X_i - \overline{X})^2 \right]^{1/2} \tag{13}$$

where $n$ is the number of experimental data of a sample, $X_i$ is the $i$th experimental point, and $\overline{X} = (1/N)\sum_{i=1}^{N}(X_i)$ is the mean value of the sample. It should be remarked that the overall uncertainty of the viscosity measurements reported is significantly greater than $2\sigma_{\mathrm{m}}$ as described before.

**Viscosity by Capillary Methods.** In the present work, viscosity measurements of the sample of $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$ were also carried out using Ubbelohde and micro-Ubbelohde capillaries. The results obtained with both capillaries are shown in Table 7, at several nominal temperatures. Each viscosity value shown is the mean value of five measurements, and the correction to nominal temperatures was performed as described above for the vibrating wire results. The flow times were greater than (480 and 240) s, respectively, so that no kinetic energy correction was necessary. The water content for the Ubbelohde capillary was (41 and 247) $\mathrm{mg \cdot kg^{-1}}$, before and after the measurements, respectively. The corresponding values for the micro-Ubbelohde capillary were (77 and 379) $\mathrm{mg \cdot kg^{-1}}$. The Ubbelohde capillary was previously calibrated using the PTB100B reference fluid,[9] as stated above, and the uncertainty of the capillary measurements is estimated as ± 1.6 %. As pointed out before, this estimate of uncertainty was made assuming a significant contribution of the difference in the surface tension of $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$ and of the liquids used for calibration of the capillaries.[30,32] This estimate is seldom observed in the literature, and it is to be noted that no mention is made in the literature data for $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$. For the measurements performed with the micro-Ubbelohde capillary, it was assumed that the uncertainty attributed to the effect of the surface tension on the results was similar to the one estimated for the conventional Ubbelohde capillary. As mentioned before, this assumption is supported by the good agreement of the results obtained by the two instruments, as shown in Table 7.

**Table 7. Mean Values of the Viscosity Measurements, $\eta$, Obtained Using an Ubbelohde Capillary and a Micro-Ubbelohde Capillary, at Nominal Temperatures, $T_{\mathrm{nom}}$, and Atmospheric Pressure of $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$**

| capillary | $T_{\mathrm{nom}}$ | $\rho^{a}$ | $\eta$ | $\sigma_{\mathrm{m}}{}^{a}$ |
|---|---|---|---|---|
| (water content after the measurement) | K | $\mathrm{kg \cdot m^{-3}}$ | mPa·s | mPa·s |
| micro-Ubbelohde (379 $\mathrm{mg \cdot kg^{-1}}$) | 298.17 | 897.99 | 372.8 | 0.07 |
|  | 303.13 | 895.14 | 282.4 | 0.04 |
|  | 308.09 | 892.31 | 217.2 | 0.04 |
| Ubbelohde (247 $\mathrm{mg \cdot kg^{-1}}$) | 303.11 | 895.14 | 284.5 | 0.16 |
|  | 317.92 | 886.78 | 135.2 | 0.05 |

[a] $\sigma_{\mathrm{m}}$ is the standard deviation of the mean value, $\eta(T_{\mathrm{nom}})$; density values at nominal temperatures, $\rho(T_{\mathrm{nom}})$, were obtained from eq 7, with parameters from Table 3.

**Estimation of the Effect of the Water Content on the Viscosity of the Samples.** The maximum uncertainty of the determination of water in our samples by Karl Fischer coulometric titration was estimated to be ± 21 $\mathrm{mg \cdot kg^{-1}}$. This estimate was based on the repeatability of the measurements and on the verification of the measurement accuracy by comparison with standard reference solutions. To estimate the effect of the water content on the viscosity of the samples of $[\mathrm{P}_{6,6,6,14}][\mathrm{dca}]$, some results of the viscosity of samples with various amounts of water contamination are shown in Table 8.

**Table 8. Viscosity Data for Samples with Various Water Contents Obtained in the Present Work**

|  | $T_{\mathrm{nom}}$ | $\eta$ | water content after the measurement |
|---|---|---|---|
| method | K | mPa·s | $\mathrm{mg \cdot kg^{-1}}$ |
| micro-Ubbelohde | 298.17 | 362.7 | 668 |
| micro-Ubbelohde (from Table 7) | 298.17 | 372.8 | 379 |
| vibrating wire (from Table 6) | 298.20 | 378.0 | 300 |
| vibrating wire | 298.19 | 379.3 | 249 |

In particular a measurement performed with the micro-Ubbelohde capillary of the viscosity of a sample that had 668 mg of water per 1 kg, after the measurement, yielded a viscosity of about 363 mPa·s, is compared in Table 8 with a datum shown in Table 7, obtained with the same method on a sample that had 379 $\mathrm{mg \cdot kg^{-1}}$ of water after the measurement. This comparison suggests that an increase of 100 $\mathrm{mg \cdot kg^{-1}}$ of water may reduce the viscosity of the sample by about 0.9 %.

In the same table, results obtained by the vibrating wire method are also shown for comparison. The viscosity of a sample containing 249 $\mathrm{mg \cdot kg^{-1}}$ of water after the measurement is compared with the result shown in Table 6, for a sample containing 300 $\mathrm{mg \cdot kg^{-1}}$. Although the difference of water content is now much smaller, a coarse estimate of that effect can be obtained. This is of the order of 0.6 % decrease of viscosity as a result of an increase of 100 $\mathrm{mg \cdot kg^{-1}}$ of water, which is comparable to the value obtained with the microcapillary. The value of 0.9 % decrease in viscosity owing to an increase in the water content of 100 mg·kg$^{-1}$ was used to estimate the effect of water contamination in the viscosity of the [$P_{6,6,6,14}$][dca].

**Comparison of Viscosity Results.** In Figure 6, the deviations of the results obtained in the present work using an Ubbelohde capillary and an Ubbelohde microcapillary from the correlation of the vibrating wire results are shown. The only difference among the samples used in the three sets of measurements is the water content before and after the measurements. Nevertheless, those differences are not very significant (using the estimates given earlier) and should not give rise to any relevant discrepancy between the viscosities of the samples. The results obtained with the two different capillaries used in the present work at around 303 K are in very good agreement, the difference being less than 0.8 %, well within their uncertainty. The viscosity capillary results are all lower than those obtained with the vibrating wire method. The deviations found between the capillary and the vibrating wire measurements are not greater than 2 %, which is commensurate with the estimated overall uncertainty of each of the vibrating wire results. It is, of course, to be expected that the deviations are systematic given the sources of the greatest uncertainties.

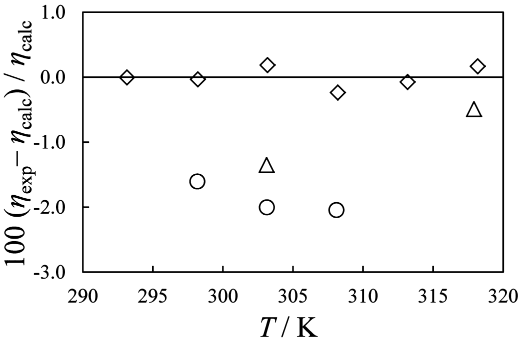

**Figure 6.** Deviations of the viscosity results for [$P_{6,6,6,14}$][dca], obtained in the present work with the vibrating wire method; ◇ (nominal values from Table 6); with the Ubbelohde capillary, ○, and with the Ubbelohde microcapillary, △, techniques, from the correlation of eq 10 with the parameters of Table 5.

One set of viscosity data of [$P_{6,6,6,14}$][dca] has been found in the literature. The capillary viscometer measurements have been carried out by Pereiro et al.[33] at temperatures $T$ = (293.15 to 343.15) K, using a commercial measuring unit PVS1 from Lauda, and have indicated an estimated uncertainty of 2 %. The sample was the same that those authors used for the density measurements mentioned above, the content of chlorides being less than 205 mg·kg$^{-1}$. The water content was 125 mg·kg$^{-1}$ (measured with a Metrohm KF 831 coulometer) before the measurements, and it was reported to have increased 400 mg·kg$^{-1}$ during the measurements. The deviations of the results obtained by those authors from the correlation of the present measurements performed with the vibrating wire instrument are shown in Figure 7, together with the results obtained in the present work. It is to be noted that, although the water content reported by Pereiro et al.[33] is higher than the one we measured in our samples, their data is systematically higher than our results. This kind of deviation might be explained by the higher chloride content of their sample. In fact Seddon et al.[10] have shown that the content of chloride ions in ionic liquid samples increases the viscosity very significantly while the opposite effect in the density is observed but much weaker. However, Pereiro et al.[33] reported a chloride content of 205 mg·kg$^{-1}$, as determined by potentiometry. This numerical value is similar to the content of our sample (200 mg·kg$^{-1}$ by HPLC) so that it is not clear that the chloride content can explain the discrepancy between the two sets of data. The commercial measurement method used by those authors and the protocol of its usage are not described in detail, and there is simply not enough information to examine the reliability of the results they obtained. We are unable to offer any explanation for the difference of their viscosity data from ours.

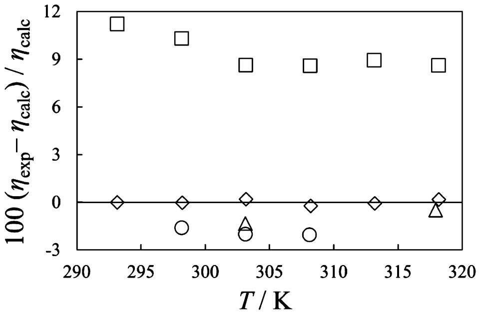

**Figure 7.** Deviations of the viscosity results for [$P_{6,6,6,14}$][dca], obtained by Pereiro et al.,[33] □, and in the present work using: the vibrating wire technique, ◇ (nominal values from Table 6); an Ubbelohde capillary, ○, and an Ubbelohde microcapillary, △, from the correlation eq 10 with the parameters of Table 5.

## ■ CONCLUSIONS

New viscosity measurements of ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide [$P_{6,6,6,14}$][dca] were made using the vibrating wire technique, at atmospheric pressure. Several tests were performed and have demonstrated the applicability of the method with this ionic liquid.

Density measurements were carried out using a U-tube Anton Paar density meter. One of the data sets found in literature differs about +2.5 % from our fitting equation, and the other one has a systematically higher deviation to the present results, within +0.1 %, which is commensurate with the estimated uncertainty of our measurements.

The only viscosity literature data set that could be found deviates from the viscosity results presented in this paper by more than the nominal uncertainties of our vibrating wire measurements which were compared with measurements made using a calibrated Ubbelohde capillary and an Ubbelohde microcapillary viscometers. It was shown that all of the viscosity data presented here agree within the estimated uncertainty of ± 2 % of the vibrating wire measurements. This is strong evidence to support the contention that the viscosity data reported here are more likely to be correct than those derived from an unvalidated experiment.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

(S.1) Preparation and characterization of trihexyl(tetradecyl)-phosphonium dicyanamide. (S.2) Vibrating wire frequency response for different external noise levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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