

17 Accurate Measurement of Physicochemical Properties on Ionic Liquids and Molten Salts

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Abstract

The measurement of physicochemical properties of liquids has proved a difficult task, especially if the measurements are to be performed in temperature and pressure ranges far from the ambient conditions and if the liquids have properties that make it difficult to mathematically model the instrument to be used. Even for molecular liquids, where the interactions in the liquid state are essentially known and easier to characterize, it is still difficult to measure properties with high accuracy. Ionic liquids, made of isolated or aggregated ions, are electrically conducting, polarizable, and almost nonvolatile, posing several problems for the design and use of standard equipment. They cover a very wide temperature range, from LTILs to HTILs (molten salts). It is the purpose of this chapter to analyze the measurement of several thermophysical properties—namely, viscosity, thermal conductivity, electrical conductivity, electrical permittivity, and binary diffusion of water—using our previous experience in measurements of molecular liquids, electrolyte solutions, and molten salts.

17.1 INTRODUCTION

Ionic liquids (or low temperature molten salts) are considered today to constitute a class of liquids with the highest potential to revolutionize the chemical industry, as they constitute innovative fluids for chemical processing, which are generally nonflammable and nonvolatile under ambient conditions and thus perceived as “green” solvents. However, to implement new processes, it is necessary to prove that they are competitive with the traditional processes, not only from the point of view of final products, but for all the technological operations involved in the processes.

The optimal technological design of green processes requires the characterization of the ionic liquids used. The recent explosion in research and applications of low temperature ionic liquids (LTILs) raises several problems: the need for data is growing exponentially (currently very sparse) and the number of new compounds has been estimated by Earle and Seddon [1] to be on the order of one million.

The accurate measurement of the thermodynamic and transport properties of molten salts, high temperature ionic liquids (HTILs), has proved difficult in the past [2, 3]. The particular intermolecular interactions, localized and nonlocalized, and the difficulties of adapting the existing methods of measurement to this research have created this situation. This is particularly true for the transport properties, where the mechanisms of mass, momentum, heat, and charge transfer in Coulombic liquids are far from being completely understood; this can be illustrated for viscosity, where we know how to measure it at room temperature for normal organic and inorganic liquids with an accuracy of 0.5% or better, while at high temperatures an excellent value is $\pm 2\%$, most of the times impossible to achieve.

In the following sections we analyze the similarities and differences between molten salts and “ionic liquids”, and their relationships to measurement procedures. We restrict our analysis to properties of pure ionic liquid and to the physical/chemical factors that are known to influence these properties. These are the melting points, density, heat capacity, viscosity, thermal conductivity, electrical conductivity, relative permittivity (dielectric constant), and surface tension. Diffusion in ionic liquids + water systems is also discussed, as water is very important in the purity of ionic liquids and in the solubility phenomena of complex processing mixtures.

17.2 MOLTEN SALTS AND IONIC LIQUIDS

Molten salts were the first ionic liquids to be studied experimentally. The naming resulted from the fact that they are usually crystallized salts at room temperature. Table 17.1 shows the main characteristics of molten salts and some of the additional problems for measurement. Figure 17.1 shows results obtained for the viscosity of molten LiNO_3 , from its melting point to 700 K, taken in our laboratory and by other authors [4]. It can easily be seen that there is no agreement between the different sets of data, within their mutual uncertainty, the differences between different laboratories being sometimes dramatic (10–15%), but that the curves are parallel, which indicates systematic errors in the measurements. Figure 17.2 shows the thermal conductivity

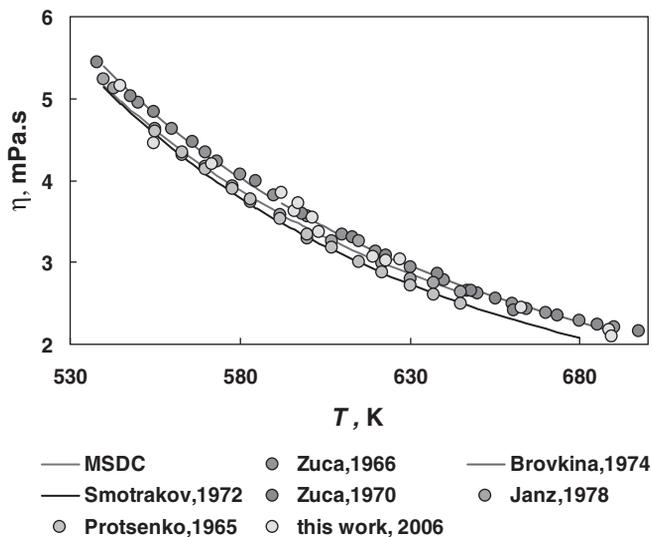
TABLE 17.1 Main Characteristics of Molten Salts and Ionic Liquids

Molten Salts	Ionic Liquids	Additional Problems
<ul style="list-style-type: none"> • Liquid state in a large temperature range • Ability to dissolve many inorganic and organic compounds, attaining high concentrations • Low vapor pressure and stability at normal pressures • Low viscosity, as the ions are mutually independent for most of the cases • Chemical inertness (no reaction with air or water) • High heat capacity per unit volume 	<ul style="list-style-type: none"> • Liquid state in a large temperature range • Ability to dissolve many inorganic and organic compounds, attaining high concentrations • Nonflammability • Low vapor pressure and stability at normal pressures 	<ul style="list-style-type: none"> • Medium and high temperatures ($T > 400$ K) • Purity of compound in the beginning of the measurements • Change in composition during measurements due to reactions (decomposition, with container and/or environment) or multiple recrystallizations • Materials compatibility between sample, crucibles, and atmosphere • Low to high viscosity, as the ions are not mutually independent for most of the cases and can form aggregates • Cations and anions have completely different sizes • Reaction with water is possible • High solubility of water in LTILs, affecting the properties • Moderate heat capacity per unit volume

of molten KNO_3 from its melting point up to 730 K. Here the situation is even worse than that found for viscosity, as the differences between different laboratories can be greater than 25% and the temperature slope of the thermal conductivity can be positive, negative, or zero! Several explanations attempt to rationalize this situation:

- The methods of measurement applied were not modeled with the correct physical model and mathematical solution.
- The mechanisms of mass, momentum, heat, and charge transfer in Coulombic liquids are far from being completely understood.
- There is a lack of calibrating fluids for the viscosity range used, namely, for capillary viscometry.

Examples of these items can be capillary viscometers, with corrections for the surface tension based on that of water; not accounting for radiation heat transfer in



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FIGURE 17.1 The viscosity of molten lithium nitrate from its melting point to 700 K, measured in our laboratory, and by others [4]. References mentioned in this caption can be found in Reference 4.

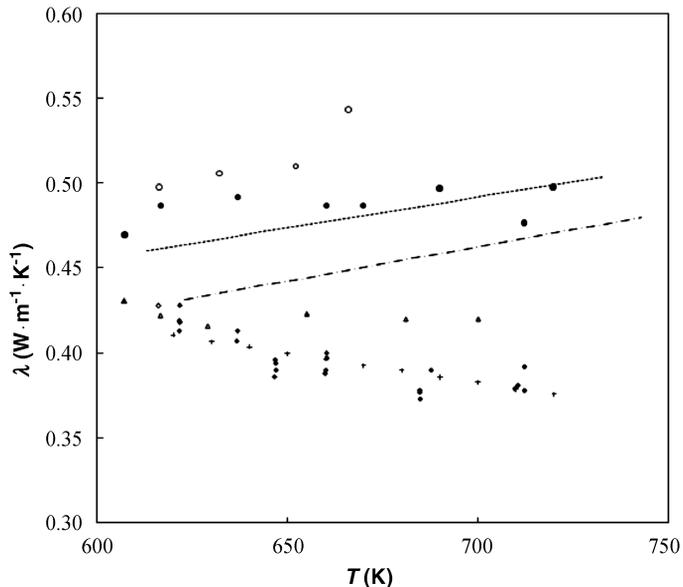


FIGURE 17.2 The thermal conductivity of molten potassium nitrate. Δ , Tufeu et al.; \blacklozenge , Kitade et al.; \circ , Bloom et al.; \blacktriangle , White and Davies; $+$, Nagasaka et al.; \bullet , Gustafsson et al.; \diamond , Turnbull; $\bullet\bullet\bullet\bullet$, McDonald and Davies; $--\bullet--$, Santini et al. References mentioned in this caption can be found in Reference 2.

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thermal conductivity measurements; and bad definition of electrical conduction paths between electrodes. From these examples, it can be concluded that the measurement situation in molten salts, especially for transport properties, did not evolve significantly for the last thirty years, that temperatures above 600 K are still a problem, and that there is an urgent need for refinement of methods of measurement.

For the case of LTILs, in spite of the low temperature range of applicability of these liquids, the situation is far from being better, not because one does not know how to make the measurements, but because a great number of problems arise. In Table 17.1, the main properties of ionic liquids are identified, mostly common to molten salts, but with some additional problems that can influence the measurements, if not accounted for. These problems can be systematized in the following manner:

- It is impossible to measure all the properties of all the liquids needed for the design of new processes and plants in a reasonable time frame.
- Some of the liquids have unusual properties, with high or abnormal values, which require reference materials for the measurement of these properties [5].
- Some of the measuring methods need to be modified to account for the ionic character of these salts.
- The nonexistence of reference or calibrating liquids for the properties needed for the chemical process design, namely, for the ranges attained for these fluids, must be resolved.
- The difficulty in having “pure” liquids for the property determination, namely, caused by their extraordinary ability to dissolve water, as well as unreacted molecular compounds from their synthesis, like chloride ions, must be resolved.
- Some of the existing knowledge can change very fast, as some recent publications show, namely, about the volatility of ionic liquids [6].
- The nonapplicability of the available property predictive methods to these compounds must be resolved.

The amount of data obtained so far for the thermophysical properties of ionic liquids does not yet have the quality that allows us to make comparisons similar to those made for the molten salts. The work is more developed in characterizing new liquids than in making replicate measurements in different laboratories of a given property or being able to analyze the mutual uncertainty of the data. However, a recent review of the properties of pure ionic liquids—restricted to melting points, density, viscosity, and electrical conductivity [5]—added to our previous experience, can provide some guidance on the actual state of the art in property measurements in ionic liquids.

17.3 PHYSICOCHEMICAL MEASUREMENTS IN IONIC LIQUIDS

17.3.1 The Actual Situation

For the *melting points*, which are known to be influenced by the charge distribution on the ions, hydrogen-bonding ability, symmetry of the ions, and van der Waals

interactions, the situation is reasonable, but the impurities in the samples can cause a freezing depression on the melting temperatures, and this has limited the use of much data, where even confusion between glass temperatures and melting points could not be avoided.

For the *density*, it is known that the great majority of LTILs are much denser than water. However, the comparison of data obtained in different laboratories for samples of [C₄mim][PF₆] showed differences of up to 3%. The case is even worse (change of sign of the temperature dependence) for the thermal expansion coefficient and for the isothermal compressibility [5]. The main reason for these discrepancies is probably purity.

Most of the ionic liquids are moderately or highly viscous, with viscosities more comparable to the viscosities of oils, two or three orders of magnitude greater than most organic solvents. This higher *viscosity* has several disadvantages, some related to its negative effect on the heat and mass transfer rates in the processes to which they were applied, others related to the fact that viscosities greater than 150 mPa·s (at 20 °C, 430 mPa·s for [C₄mim][PF₆] and 154 mPa·s for [C₄mim][BF₄]) are difficult to obtain with high accuracy, due to the lack of internationally accepted reference liquids for calibration [7] and the experimental difficulties for its absolute measurement [8, 9]. Moreover, it is well known that viscosity is one of the properties most strongly influenced by impurities, from water to halogen acids. As an example, 1% of water decreases the viscosity of [C₄mim][NTf₂] at 20 °C by 33%, and 0.1% of water decreases the viscosity of [C₄mim][PF₆] at 20 °C by 16.6% [10]. The amount of data existing for the viscosities of ionic liquids, even for less pure samples, is so scarce that a good measurement program is highly recommended [5].

These authors also recommend that the study of *electrical conductivity* is absolutely necessary. A very recent paper [11] shows that 5% of water in [C₂mim][BF₄] increases its conductivity by a factor of 3.2, a value that recommends extreme care of the sample purity during these measurements.

For the *thermal conductivity* of ionic liquids, no direct measurements were found. For *electrical permittivity* (*dielectric constant*) only measurements at high frequency (dielectric relaxation) were recently obtained. For *heat capacity*, the number of results already reported is indeed very small. For the case of *surface tension*, there have been few measurements, but it looks as if the presence of water did not significantly affect the measurements [12]. The surface tensions are lower than that of water, but higher than for linear alkanes.

The facts cited above highlight one of the most important issues to be resolved: before experimental methods of measurement (existing or to be developed) are applied to a given sample or batch of samples of ionic liquids – there must be *the guarantee of purity*. By guarantee, we mean determination by a given analytical method, with a well-known uncertainty/accuracy. Although recent advances in quantitative analytical characterization have been reported [13], it seems that further developments on the applications of several techniques are strongly needed.

The second point cited above, which has been demonstrated to influence the experimental results obtained for viscosity and electrical conductivity, is the presence of water in the ionic liquid, dissolved or chemically bonded. Both these properties are known to be strongly affected by impurities, and as mentioned before, the presence

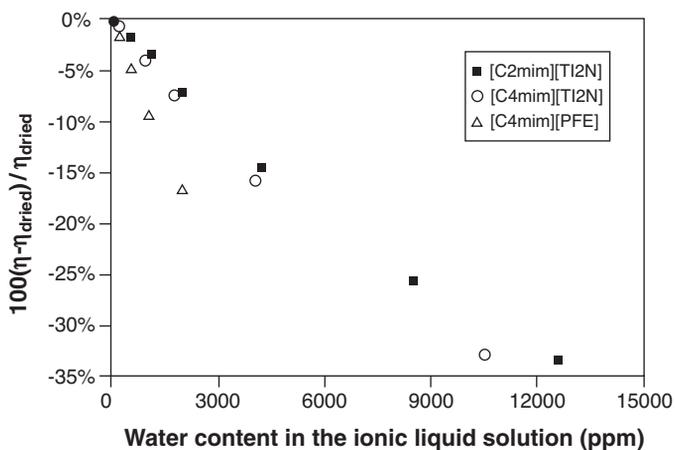


FIGURE 17.3 Percentage change in the absolute viscosity versus water content for [C₂mim][NTf₂], [C₄mim][NTf₂], and [C₄mim][PF₆] [10].

of water and organic solvents has been shown to decrease the viscosity of LTILs [14–16], and the presence of chloride has been shown to increase the viscosity of LTILs [14]. Widegren, et al. [10] noted that little is known about the quantitative effect of low levels of water on physical properties. Water is the most insidious impurity because of its ubiquity. Even “hydrophobic” LTILs, which are not miscible with water, rapidly absorb water from the atmosphere [14, 17–19] or from moist surfaces. Hence, unless an LTIL is carefully dried and handled, it will be contaminated with water. Figure 17.3 shows the percentage change in the absolute viscosity versus water content for three ionic liquids, [C₂mim][NTf₂], [C₄mim][NTf₂], and [C₄mim][PF₆], obtained by these authors [10], using a capillary open to the atmosphere, and with the water content in the sample determined before and after the measurements (a key to these experiments is that the water content of the LTIL was determined before and after each viscosity measurement by coulometric Karl Fischer titration). It can be seen that the addition of 1% (by mass) of water can decrease the viscosity as much as 30%. In addition, time facilitates the diffusion of atmospheric water (with or without chemical reaction), which justifies the measurement of the diffusion coefficient of water at infinite dilution, to better understand the influence of water on the properties of these compounds, viscosity and others. These results were confirmed in our laboratory, and in NIST, for [C₆mim][NTf₂], where 100 ppm (0.01%) of water was found to decrease the viscosity by 5%, a value much greater than the claimed uncertainty of the data. For the case of electrical conductivity, it is enough to report the data also obtained by the NIST team for four hydrophobic room-temperature ionic liquids, [C₂mim][NTf₂], [C₄mim][NTf₂], [C₆mim][NTf₂], and [C₄mim][PF₆] [20]. For water + [C₄mim][NTf₂], the electrical conductivity was found to increase dramatically with increasing $w_{\text{H}_2\text{O}}$; for example, in going from $w_{\text{H}_2\text{O}} = 10^{-5}$ to 10^{-2} , the fractional increase in κ was 0.36 ($= (\kappa_{\text{wet}} - \kappa_{\text{dried}}) / \kappa_{\text{dried}}$). This work illustrates the importance of measuring the water content in LTILs, both before and after

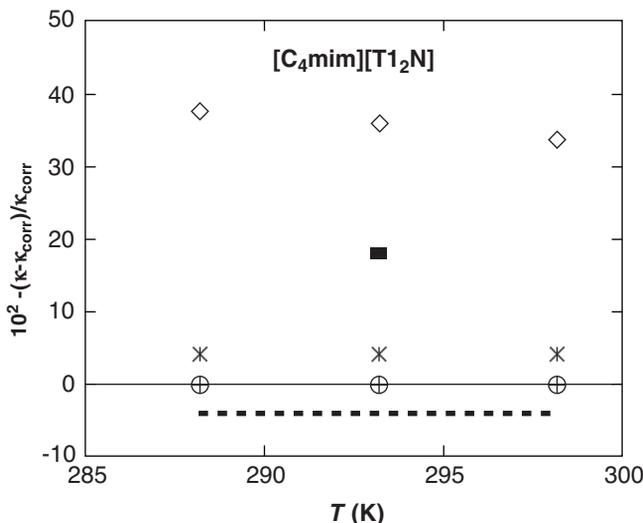


FIGURE 17.4 Plot of the relative deviations of the electrical conductivity of the mixtures $[\text{C}_4\text{mim}][\text{NTf}_2] + \text{water}$ from that of pure $[\text{C}_4\text{mim}][\text{NTf}_2]$, for different amounts of water [20]. ◇, $w_{\text{H}_2\text{O}} = 8.85 \times 10^{-3}$; *, $w_{\text{H}_2\text{O}} = 1.02 \times 10^{-3}$; +, $w_{\text{H}_2\text{O}} = 8 \times 10^{-3}$; ○, dried ($w_{\text{H}_2\text{O}} = 10^{-5}$); other symbols [20].

measurements of electrical conductivity. Figure 17.4 shows a sample of the results obtained by these authors for $[\text{C}_4\text{mim}][\text{NTf}_2]$.

From these results, we recommend that to obtain results for these properties with a credible uncertainty, it is fundamental to determine, before and after the measurements, the type and amount of impurities present; and in the case of hydrophobic LTILs,¹ it is necessary to measure the amount of water present and make the measurements under a controlled atmosphere (under flushing dry nitrogen in our laboratory).²

17.3.2 The Methods of Measurement

We restrict our analysis of the methods of measurement to properties for which the group has experience: viscosity, thermal conductivity, electrical conductivity, electrical permittivity (dielectric constant), diffusion coefficients, and heat capacity. However, for this last property, no special problems additional to those encountered for nonionic liquids are envisaged. Information about the different methods used to measure the heat capacity in liquids can be found in recent works [21, 22], namely, the measurement of $[\text{C}_6\text{mim}][\text{NTf}_2]$ with adiabatic calorimetry [23].

¹For the case of HTILs, the measurements are usually made above 400 K, which makes the presence of water negligible, except in some systems.

²This procedure has proved to be insufficient, as the amount of water in the samples used to measure viscosity increased from 119.3 to 196.4 ppm during the measurements.

Viscosity 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 (T, P) or (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 damage 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, namely, the availability of a working equation and a complete set of corrections, we must require that the rates of shear are small enough to maintain a near equilibrium state and that hydrodynamic stability is maintained. Several measurements performed so far are grossly inaccurate due to the disregard of one or several of these conditions. Strictly speaking, there is no primary method³ at present for the measurement of the viscosity of liquids, as the absolute methods developed so far, in order to achieve high accuracy, involve the use of instrumental constants obtained through experimental calibration. However, the analysis of such methods [7, 8, 24, 25] (designated as relative or secondary) shows completely different 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 some of these parameters must be obtained accurately 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, cylinder, and sphere), the vibrating wire, the torsionally oscillating quartz crystal, and surface light scattering spectroscopy (SLS) methods [8]. The data obtained with these state-of-the-art instruments have smaller uncertainties (or greater accuracies), when compared with data obtained using other secondary methods, namely, the capillary viscometer (in any of its versions), the rolling ball viscometer, or the falling ball viscometer, whose calibration parameters do not possess a clear physical meaning. A complete discussion about the details and application of these methods can be found in previously referenced papers Reference 8 being more detailed about the quality of the measurements performed with the different methods. Results of the application of the oscillating cup to molten alkali nitrates can be found in References 26–28.

The application of such methods to the measurement of viscosity of ionic liquids needs some discussion, because these viscosities are moderate or high on the scale of viscosity (1 mPa s to 1 Pa s). Figure 17.5 shows the availability of calibrating liquids for the different ranges of the viscosity scale (excluding non-Newtonian

³The definition of a primary method was approved by CCQM (Comité Consultatif pour la Quantité de Matière, BIPM) 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.”

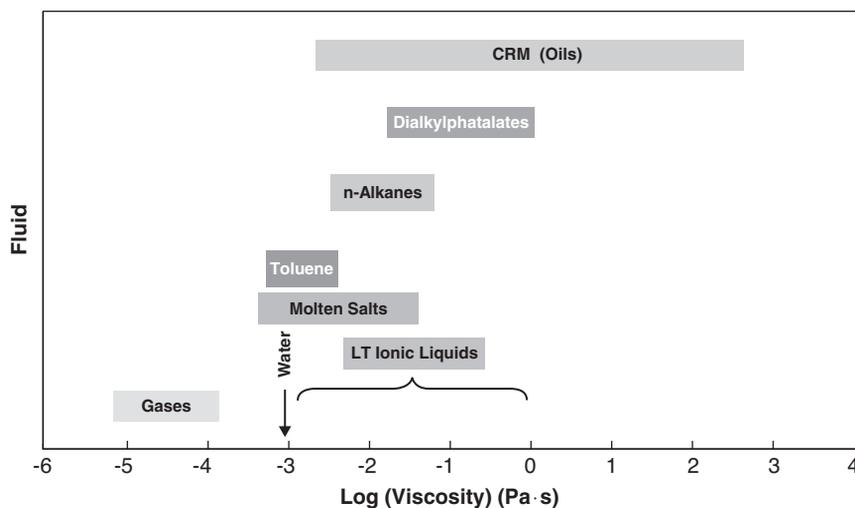


FIGURE 17.5 Viscosity ranges for different reference materials. Also shown are the viscosity domains for molten salts and LTILs.

fluids), some of them not yet used in common calibration procedures for relative viscometers. The ranges for LTIL and HTIL viscosities are also displayed, and it can be seen that they fall in a range with toluene (already accepted as a certified reference material [8]), alkanes, and alkyl phthalate esters, these last not yet approved as international standards,⁴ as there is not available a consistent set of fluids and viscosity data to justify their choice, except for diisodecyl phthalate [29]. These fluids were proposed by the authors to resolve the problem of not having primary methods of measurement of viscosity available. The traceability to SI units, always necessary, 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 much higher than the current route based only 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 installed, can avoid the higher uncertainties of the calibrations for high viscosity fluids, and the chemical limitations of pure water, previously discussed. This procedure would resolve most of the existing problems in measuring viscosity of ionic liquids.

Table 17.2 shows the most accurate methods of measurement of viscosity, their type, attainable uncertainty, and their adaptability to measure the viscosity of LTILs. From this analysis we recommend the use of quasi-primary instruments, such as the oscillating body (disk, cup, cylinder, and sphere) and the vibrating wire for high quality work (these viscometers are expensive, as they need a very accurate body machining, and should be used mostly for measuring the viscosity of well chosen

⁴From the end-user's point of view, the only viscosity reference point accepted so far is the viscosity of pure water at 20 °C, as recommended by ISO/TR 3666:1998(E), and accepted by IUPAC and OIML.

TABLE 17.2 Existing Methods for the Measurement of Viscosity and Their Applicability to LTILs

Adaptability to LTILs					
Method	Type	Attainable Uncertainty ^a	Yes	No	Maybe if
Oscillating disk	Quasi-primary	1%	For low to moderate viscosity liquids		Disk/plates edge effect corrections became available for high viscosity liquids.
Oscillating cup or cylinder	Quasi-primary	1–2%	For low to moderate viscosity liquids		Meniscus effect must be avoided for high viscosity liquids
Vibrating wire	Quasi-primary	1%	✓		
Torsionally oscillating quartz crystal	Quasi-primary	1%		✓	Correct electrical insulation of gold electrodes deposited on the crystal can be achieved without loss of performance
Surface light scattering spectroscopy	Quasi-primary	<2%	For low to moderate viscosity liquids		Possible to extend to high viscosity liquids, as the vapor pressure of the LTILs is almost negligible
Capillary flow	Secondary/relative	1–3%	For low to moderate viscosity liquids	For high viscosity liquids	The traceability chain is kept with low uncertainty
Falling body	Secondary/relative	2–5%		✓	Not recommended for high quality work

^a Uncertainty is defined using ISO criteria, using a coverage factor ($k=2$), that correspond to a 95% confidence level.

reference liquids), and surface light scattering spectroscopy methods, and capillary flow viscometers for current laboratory work. In this last case, the users must be aware of all the problems already mentioned about calibrating liquids and traceability chain to SI units.

Thermal Conductivity The thermal conductivity of a fluid measures its propensity to dissipate energy, when disturbed from equilibrium by imposition of a temperature gradient. However, thermal conductivity is one of the thermophysical properties that is difficult to measure accurately. The main difficulty lies in the isolation of pure conduction from other mechanisms of heat transfer, like convection and radiation, a fact that arises from the contradictory requirement of imposing a temperature gradient on the fluid while preventing its motion. The imposition of a temperature gradient in a fluid in the gravitational field of Earth⁵ inevitably creates a state of motion (natural convection). For isotropic fluids, the thermal conductivity is defined by Fourier's law and depends on the thermodynamic state of the fluid prior to the perturbation, and must be related with a reference state, not necessarily equal to the initial one. As it is impossible to measure local fluxes and local gradients [24], the Fourier equation cannot be used directly, and the energy equation adapted to a given geometry is the solution. However, the full energy equation cannot be used, and some approximations have to be introduced. In the first place, we must assure that the perturbation to the state of equilibrium (temperature gradients) is small, so that a near equilibrium state is maintained. Second, fluid movement must be avoided or reduced to a negligible level. It is therefore necessary to make measurements in such a way that the effect of convection is rendered negligible. Finally, it is important to recognize that the transport of energy by radiation is always present and must be corrected for each measuring technique, especially if measurements are performed at high temperatures. The full energy equation can be simplified [24] to give

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$$\rho C_P \frac{\partial T}{\partial t} = \lambda \nabla^2 T \quad (17.1)$$

where ρ is the fluid density and C_P is its isobaric heat capacity.

In the last forty years, a variety of experimental methods have been developed, for gaseous, liquid, or supercritical phases, over a wide range of thermodynamic states. These methods are based on the simplified energy equation (17.1) and can be classified into two main categories:

- Unsteady state or transient methods, in which the full equation (17.1) is used, and the principal measurement is the temporal history of the fluid temperature
- Steady-state techniques, for which $\partial T/\partial t = 0$ and the equation reduces to $\nabla^2 T = 0$, which can be integrated for a given geometry

⁵Several efforts to measure the thermal conductivity under microgravity conditions showed that we can obtain convection-free measurements. However, the cost of experiments in parabolic flight rockets, in a space shuttle, or in the ISS impedes its routine use. Only experiments designed to prove underlying principles, if financed, can be undertaken [44].

Transient methods are the only ones that can compete for the statute of primary methods, in the sense of CIPM. These methods include the transient hot-wire, the transient hot-strip, and the interferometric technique (adapted to states near the critical point). Details of these methods can be found in References 25, and 30–32. Reference must also be made to three methods for the determination of thermal diffusivity, $\alpha = \lambda/\rho C_p$, which are not direct measurements of thermal conductivity, needing accurate values of density (usually available) and heat capacity (more difficult to obtain): photon-correlation spectroscopy [32], the forced Rayleigh scattering method [33], and the transient grating technique. The first of these is a very versatile (amenable to improvement) method, the second has been applied to molten salts [33], and the third constitutes the only reported measurements so far for the thermal conductivity of LTILs [34]. Details of the forced Rayleigh scattering method and of photon-correlation spectroscopy, both based on light scattering by the material under study, can be found in Reference 25.

From all these methods, only the transient hot-wire can be considered today as a primary method [35]:

- The transient hot-wire technique was identified as the best technique for obtaining standard reference data (Certification of Reference Materials).
- It is an absolute technique, with a working equation and a complete set of corrections reflecting the departure from the ideal model, where the principal variables are measured with a high degree of accuracy. It is accepted by the scientific community as a primary method, the top of the traceability chain for this physical quantity.
- The liquids proposed by IUPAC (toluene, benzene, and water) as primary standards for the measurement of thermal conductivity were measured with this technique with an accuracy of 1% or better.

The theory of the transient hot-wire is well known [36], and a complete uncertainty analysis has been presented previously [36, 37]. The transient hot-wire method is an absolute method, where the thermal conductivity of a fluid is evaluated by monitoring the rate at which the temperature of a thin wire increases with time after a step change of voltage has been applied to it. The constant heat flux per unit length thus generated by a linear source has the effect of producing throughout the fluid a temperature field that increases with time. Details of its applications to nonconducting fluids can be found in References 36, 38, and 39. This method has also been applied to electrically conducting liquids in the past, including polar liquids, molten salts, electrolyte solutions, molten metals, and molten semiconductors. LTILs fall into this group and we shall describe its application in more detail.

When the ordinary transient hot-wire is applied to measure the thermal conductivity of electrical conducting liquids, several problems are encountered [25, 36]:

1. The contact between the bare metallic wire and the conducting liquid provides a secondary path for the flow of current in the cell, and the heat generation in the wire cannot be defined unambiguously.

2. Polarization of the liquids occurs at the surface of the wire, producing an electrical double layer.
3. The electrical measuring system (an automatic Wheatstone bridge) that detects the changes in the voltage signals in the wire is affected by the combined resistance/capacitance effect, caused by the dual path conduction.

Two main solutions have been developed to overcome these problems. One is the production around the wire of an electrical insulating coating, by direct coating with a polyester insulating layer, as developed by Nagasaka and Nagashima [40], by coating probes with ceramic for high temperature measurements, like Kitade et al. [41], or by anodizing a metallic wire at its surface, producing a very stable and thin metallic oxide insulation, like Alloush et al. [42]. When coated wires are applied, one needs to account for the thermal effects of the insulating layer, and this can be consulted in References 36, 38 and 40. The second solution, or polarization technique, consists in polarizing, with a direct current (DC) of high impedance, the wire against the cell wall. Its first application was developed in London [43] with chlorobenzene and applied systematically in Boulder [44, 45] and Lisbon [46–48] to environmentally acceptable refrigerants, all polar liquids, with significant dipole moments. As it was almost impossible to obtain samples of these fluids with high purity, the presence of small amounts of water increases drastically the electrical conductivity of the polar liquid and its capacity to dissolve small amounts of ions, always present in the cells, generating a small voltage difference between the cell walls and the bare metallic wires (usually platinum). The application of a potential between the wires and the cell walls creates electric double layers near the surface of the wires—Stern layers [49]. These double layers contain solvated ions, with a charge opposite to the metallic surface, to maintain the solution's electroneutrality, therefore screening the ions from contact with the surface charges in the wires. Current cannot flow from the wire to the cell wall, through the liquid, because the wires are “electrically” insulated. Figure 17.6 illustrates this phenomenon. Any of these solutions permits the measurement of the thermal conductivity of polar liquids with accuracies comparable to those obtained with nonpolar or nonconducting liquids, and consequently can be applied to LTILs.

The steady-state techniques comprise essentially two types of geometry: the parallel plates and the concentric cylinders. These instruments, although mostly of the absolute type, can be considered as either primary or secondary. Again, details of the different solutions can be found in References 24 and 25. The most popular (and accurate) geometry for liquids is the concentric cylinders method, where the liquid stays inside the annular gap defined by the cylinders. As in all steady-state instruments, the determination of the gap between the cylinders is crucial, and the most acute determinations are made using capacity measurements of the dielectric. An application of the method to the measurement in pure molten salts and salt mixtures has been reported by Tufeu et al. [50], for $\text{Na}[\text{NO}_3]$, $\text{K}[\text{NO}_3]$, and $\text{Na}[\text{NO}_2]$, the equimolar mixture ($\text{KNO}_3 + \text{NaNO}_3$), and HITEC.⁶ In this cell the contribution of

⁶HITEC, or HTS, is a ternary mixture (0.07 $\text{NaNO}_3 + 0.4 \text{NaNO}_2 + 0.53 \text{KNO}_3$), weight %.

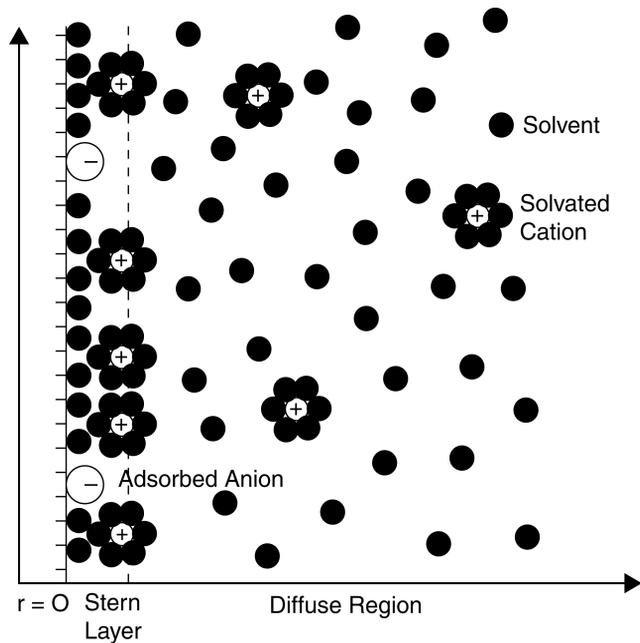


FIGURE 17.6 Model for the electric double layer on the surface of the hot-wires.

radiation to the overall heat transport was minimized by reducing the annular gap to 0.2 mm and using silver as the cylinder's material (low emissivity). The application of the steady-state concentric cylinders method to LTILs is possible, even with greater annular gaps, as the temperature can only go to its degradation temperature, usually on the order of 100–150 °C.

The use of secondary measuring techniques to measure thermal conductivity, those that need calibration with reference liquids of known thermal conductivity, is well supported, except for the high temperature range [35]. The two main works were endorsed by IUPAC and refer to the thermal conductivity of water, at 0.1 MPa, for temperatures between 275 and 370 K [51], and toluene for temperatures between 189 and 553 K [52], along the saturation line. However, for accurate work, the user should follow the discussion presented in Table 17.3, where the principal methods of measurement are analyzed, keeping in mind their applicability to the LTILs. From the only results obtained with the transient grating technique [34], the thermal conductivity of $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{NTf}_2]$, and $[\text{C}_2\text{mim}][\text{NTf}_2]$ at 298.15 K is about 100–160 $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, a value similar to most organic liquids, so no additional problems are to be encountered in using the methods displayed in Table 17.3.

Electrical Conductivity Electrical conductivity (also referred to as electrolytic conductivity) is a measure of a material's ability to conduct an electric current, usually employed as an indicator of the material's purity. The state-of-the-art primary

TABLE 17.3 Existing Methods for the Measurement of Thermal Conductivity (Thermal Diffusivity) and Their Applicability to LTILs

Method	Type	Attainable Uncertainty	Adaptability to LTILs		
			Yes	No	Maybe if
Transient hot-wire for conducting liquids	Primary	1%	✓		
Transient hot-strip for conducting liquids	Primary/secondary	1–2%	✓		Can be considered primary if the 3D heat transfer equation is solved for the geometries involved
Steady-state parallel plates	Primary/secondary	1–2%	✓		Recommended for special applications to critical states, critical end points
Steady-state concentric cylinders	Primary/secondary	2%	✓		
Forced rayleigh scattering	Secondary/relative	2–3%			Dyes necessary to enhance the signal are compatible with LTILs
Photon correlation spectroscopy	Secondary/relative	2–3%	✓		Not recommended for high quality work
Transient grating	Secondary/relative	3–5%	✓		Needs a big improvement in the calibration; not recommended for high quality work

measurement method uses cells, of parallel or concentric electrodes with variable spacing, which inhibit electrolytic conduction paths other than the direct way between electrodes, and allows the compensation of fringe effects. To ensure maximum reproducibility, avoiding the consequences of the difference in thermal expansion coefficients, cell materials are currently shifting from the classic pair of glass and platinum to ceramic and platinum thin films on ceramic. Routine measurements (temperatures between 0 and 100 °C at atmospheric pressure) still use standard platinum electrodes, although glass is sometimes replaced by suitable polymers like polypropylene [53, 54]. Primary measurements are usually done at the metrological institutes, like PTB, DFM, and NIST, among others.

Electrical measurements are performed with alternating current (AC) meters or bridges at frequencies of at least 250 Hz, usual values being 1 or 10 kHz. However, at the surface of the electrodes, polarization phenomena can occur, which influence the measured values. To avoid this error, different measuring techniques can be applied, namely, the use of a higher frequency, the use of four electrode measurements as in platinum resistance thermometry (voltage and current leads), or making inductive or capacitive nonconductive coupling between the electrodes and the measuring instrument.

Electrolytic conductivity is disseminated through the use of primary standards that are aqueous solutions of known potassium chloride concentration [55–57]. The electrolytic conductivity values were originally measured by Jones and Bradshaw, in 1933 [58], on the *demal* scale (equivalents per cubic decimeter), established by Parker and Parker in 1924 [59]. Beginning in 2001, IUPAC made the transition to the more common molality scale based standards, to account for all the effects caused by the improvement in the determination of all the involved physical constants, change of temperature scale, avoidance of the errors associated with volumetric procedures, and so on [60, 61].

The existing practice established to deal with the more common ions (mostly inorganic and usually small) is suitable to deal with most HTILs, but no real experience exists in dealing with the very large ions present in LTILs. Nevertheless, the large size of the ions in LTILs and the expected low ionic mobility might allow the use of lower measurement frequencies without the occurrence of polarization effects. High accuracy work (primary methods) will usually involve doing measurements at several frequencies and calculating the resistance from

$$R = \lim_{1/f \rightarrow 0} \Delta R(f)$$

while routine work (end-user measurements) will just use the values measured at the standard frequency of the measuring instrument, after having calibrated the measurement cell with secondary reference solutions of electrolytic conductivity [54, 57].

For LTILs and HTILs, this property is strongly dependent on temperature and viscosity, and moderately dependent on pressure, with most available studies being on the temperature effect [62, 63]. However, the presence of water is a major concern, as in other properties, because the electrical conductivity of ionic liquids is strongly affected by its presence, even at the low ppm range [20]. Figure 17.4 shows the relative deviations of the electrical conductivity of the mixtures ($[\text{C}_4\text{mim}][\text{NTf}_2] + \text{water}$)

TABLE 17.4 Existing Methods for the Measurement of Electrical Conductivity and Their Applicability to LTILs

Method	Type	Attainable Uncertainty	Adaptability to LTILs		
			Yes	No	Maybe if
AC impedance method	Primary	0.1–0.5%	✓		
Impedance method, DC or AC, using four electrodes	Primary/ secondary	0.5–1%	✓		
Resistance or conductance method, with cell constant determined by calibration	Secondary/ relative	1–3%	✓		Needs a big improvement in the calibration; not recommended for high quality work

from that of pure $[C_4mim][NTf_2]$, for different amounts of water, obtained by Widegreen et al. [20], who used an AC impedance bridge technique to measure σ as a function of temperature at about 0.1 MPa, using a commercial cell made of borosilicate glass with two platinum black electrodes, calibrated with standard potassium chloride solutions, with an uncertainty of 2% in σ . The effect of increasing the water content is dramatic and increasing w_{H_2O} by only 2.5×10^{-4} increased the electrical conductivity by 1%. Table 17.4 shows the applicability of the electrical conductivity measurements to LTILs.

Electrical Permittivity The measurement of the electrical permittivity relative to vacuum (dielectric constant) allows the study of fluid molecular behavior when subjected to an electric field, related to chemical structure and molecular interactions. The measurement of the properties of dielectrics has been the subject of multiple investigations in the past, and the general principles are reasonably established and understood [64–67]. However, when developing new materials for new applications, as in the case of ionic liquids, it is necessary to measure experimentally the dielectric constants as a function of temperature and density in order to understand their electronic structure and behavior. The response of the different materials to an applied electrical field, of frequency ν , can be characterized by the complex electrical permittivity $\tilde{\epsilon}(\nu)$, given by [64, 65]

$$\tilde{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) = \epsilon^\infty + \Delta\tilde{\epsilon}(\nu) + \frac{\sigma}{i2\pi\nu\epsilon_0} \quad (17.2)$$

The real part $\epsilon'(\nu)$ reflects the dielectric dispersion and it is usually decomposed into the frequency-dependent contribution $\Delta\tilde{\epsilon}(\nu)$ and a high frequency contribution ϵ^∞ due to the electronic and nuclear displacement polarizations in the infrared and

optical regimes. The static dielectric constant, ε , is defined as the zero-frequency limit of the dispersion curve:

$$\varepsilon = \varepsilon^\infty + \lim_{\nu \rightarrow 0} \Delta \tilde{\varepsilon}(\nu) \quad (17.3)$$

The imaginary part, $\varepsilon''(\nu)$, reflects dielectric absorption or loss, important for studying relaxation processes in the liquids, amenable, inter alia, by microwave dielectric spectroscopy (or dielectric relaxation spectroscopy) [68, 69] and electrochemical impedance techniques [70]. In addition to the relaxation contribution, the absorption spectrum is superimposed by a diverging low frequency response proportional to the static (DC) electrical conductivity of the sample, σ . This term becomes very important at low frequencies and for highly conducting liquids—see Eq. (17.3)—a fact that has to be very well analyzed for measurements in ionic liquids.

Q4

Measurements of the dielectric constant have been performed in the past for several liquids, liquid mixtures, and complex materials. In the case of liquids, however, the number of groups that measured dielectric constants in recent years is very limited, and normally restricted to the measurement of the static dielectric constant, measured usually at frequencies⁷ between 1 and 100 kHz, well below of the 1 MHz to 20 GHz of the microwave spectroscopy measurements. In this region, the dielectric constant of polar molecular liquids is frequency independent, as shown by Mardolcar et al. [71] for toluene and benzene (1 kHz and 10 kHz), where the values at the same temperature never differ by more than 0.05%. A long series of measurements in environmentally acceptable refrigerants (pure, binary, and ternary mixtures) was recently reviewed by the authors [72], with uncertainties never exceeding 0.16%, including the uncertainty caused by the sample purity (1 part in 10³). This last work was based on an instrument designed and constructed to operate in an extended thermodynamic range, from 170 K up to 370 K, at pressures up to 30 MPa. The measurements use the direct capacitance method. The description of the cell, based on two concentric cylinders, with a gap of 0.1 mm and 10 cm long, has been presented before by Mardolcar et al. [71] and the sample handling, vacuum, and pressure system are described by Gurova et al. [46]. The measuring process uses fully automated instrumentation, operated from a computer graphics user interface, and described elsewhere [73]. Vacuum capacitance was measured as a function of temperature before filling the cell with the fluid. The technique employed a four-terminal connection to the cell, in order to compensate for parasitic impedances. The mean value of a 10-dimensional sample, taken at a 10 kHz frequency, provides the experimental value of relative permittivity, which proved to be properly suited to the working accuracy. The relative permittivity, ε , of the fluid is determined from the ratio between $C(P, T)$ —the geometric capacitance at pressure P and temperature T —and $C_0(T)$ —the capacitance under vacuum at a temperature T :

$$\varepsilon = \frac{C(p, T)}{C_0(T)} \quad (17.4)$$

⁷Usually, for normal liquids, a frequency between 1 and 100 kHz is enough to make the frequency high enough to avoid the dielectric relaxation.

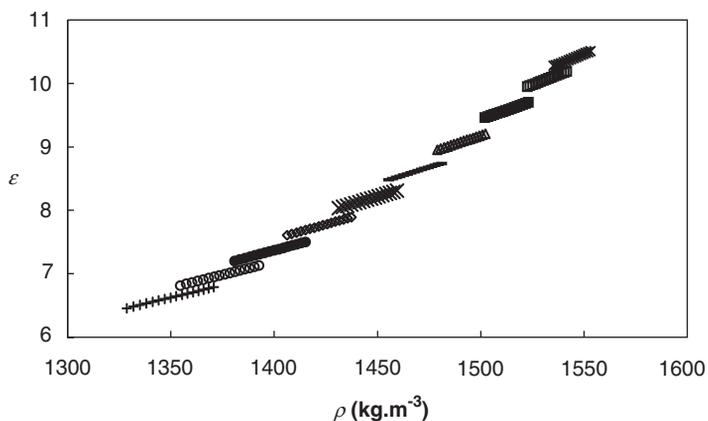


FIGURE 17.7 The relative permittivity ϵ , of 1,1,1,3,3-pentafluoropropane, as a function of density, ρ , for the different isotherms. +, 303.84 K; \circ , 293.23 K; \bullet , 283.19 K; \diamond , 273.12 K; \times , 263.00 K; $-$, 253.01 K; Δ , 243.02 K; \blacksquare , 233.12 K; \square , 224.16 K; $*$, 218.53 K [72].

Figure 17.7 displays the results obtained for 1,1,1,3,3-pentafluoropropane for temperatures between 218.53 and 303.84 K, as a function of density. All the fluids studied showed dielectric constants varying between 5 and 30, covering what are usually considered to be fluids of low to high polarity. In fact, some of these fluids are strongly polar, showing cooperative polarization effects typical of hydrogen bonding systems, as proved by Cabral et al. [74] for difluoromethane (HFC-32), 1,1,1,2-tetrafluoroethane (HFC-134a), and 1,1,1-trimethylethane (HFC-143a). The method of electrochemical impedance spectroscopy is similar, as it can use an AC stimulus, in the form of a voltage (one measures the current response) or of a current (in this case one measures the voltage response). For dielectric constant measurements, the use of voltage excitation is more common, if the voltage used is well below the decomposition potential of the liquid under study [70, 74]. A special cell was developed by these authors, prepared to measure the electrical properties of highly resistive liquids, using parallel plate electrodes, with a large ratio of electrode area to interelectrode gap, using multiple, closely spaced, parallel plate electrodes, of an air variable capacitor. Measurements with the binary system (butanenitrile + chloroethane) showed values of the dielectric constant varying from 13 (pure chloroethane at 238 K) to 45 (pure butanenitrile at 170 K). The uncertainty of the measurements is on the order of 0.5, which can make the uncertainty on the order of 1–4%, a value that reflects the need for further improvement.

The use of microwave dielectric spectroscopy in the measurement of the dielectric constants of LTILs started recently and has been implemented by Weingärter and co-workers [68, 69]. A very recent paper [71] discusses the values obtained from 14 LTILs, with imidazolium, pyrrolidinium, pyridinium, and ammonium cations, and fluorometallate, triflate, and bis[(trifluoromethyl)sulfonyl]amide anions at 298.15 K, with an uncertainty better than 0.6%. As the reported values of the dielectric constants

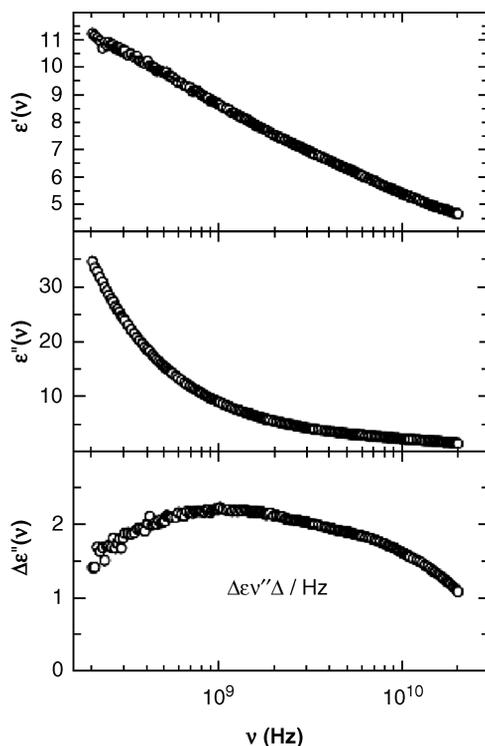


FIGURE 17.8 Real part (negative), imaginary part, and conductance-corrected (negative) imaginary part of the complex permittivity of $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 298.15 K [69].

of these liquids have values between 10 and 15.1, the uncertainty can amount to 4–6%, a value that is still high and justifies improvement of the method. At this level of uncertainty, the amount of impurities present in the samples and the possible absorption of water cannot play a relevant role. Figure 17.8 displays the real part (negative), imaginary part, and conductance-corrected (negative) imaginary part of the complex permittivity of $[\text{C}_4\text{mim}][\text{NTf}_2]$ at 298.15 K.

From the discussion above, it is clear that only the direct capacitance method can be considered a primary method for measuring the dielectric constant of polar liquids. It is an absolute method, not needing any type of calibration. Its application to ionic liquids and the complete study of the interaction between the ion mobility and the polarization in the ionic liquid are under study, but if a careful design of the cell is obtained [75], no special impediments are foreseen. The other two methods—electrochemical impedance spectroscopy and dielectric relaxation spectroscopy—still need some improvement and therefore are considered for now as secondary methods. Table 17.5 resumes this discussion. As a main conclusion, all the methods mentioned can be applied to the measurement of the static dielectric constant of LTILs.

TABLE 17.5 Existing Methods for the Measurement of Electrical Permittivity and Their Applicability to LTILs

Method	Type	Attainable Uncertainty	Adaptability to LTILs		
			Yes	No	Maybe if
Direct capacitance method (concentric cylinder electrodes)	Primary	0.2–1%	✓		
Electrochemical impedance spectroscopy, voltage driven (multiple parallel plates)	Primary/ secondary	1–4%	✓		Can be improved to primary method if a detailed analysis of the current flow between electrodes is made [K]
Dielectric relaxation spectroscopy	Secondary	4–6%	✓		Improvements of the technique are necessary; permits the full frequency spectrum dielectric response

Q5

Diffusion Coefficients The diffusion process in liquids is by far one of the most difficult transport phenomena, and can be simply defined as the process whereby an initially nonuniform distribution of species in a mixture proceeds toward a uniform distribution [25, Chap. 9]. The main problems rely on the misinterpretations that affect the discussion about the quality and comparability of the different methods of measurement. Therefore it is necessary to start with some definitions to clarify the issue, namely, those of the self-diffusion coefficient, the interdiffusion (or mutual diffusion) coefficient, and the intradiffusion coefficient. Following, for the sake of consistency, the definitions in Reference 25, the *self-diffusion coefficient* is the coefficient obtained in a system where there is only one component in diffusional motion, and can be studied by techniques like nuclear magnetic resonance. The *interdiffusion coefficient*, the most popular and analyzed coefficient because it is the fundamental one in a diffusion process in binary or multicomponent diffusion, appears when there is simultaneous diffusion of several species, where the molar fluxes of the different species are not completely independent but obey the overall continuity equation, in molar quantities [76]. For a binary mixture, the most common case, in the absence of chemical reaction and net movement of the liquid mixture (no mass convection), and when the product $c \mathcal{D}_{AB}$ can be considered constant, the equation of continuity for the mixture reduces to

$$\begin{aligned}
 \frac{\partial c_A}{\partial t} &= \mathcal{D}_{AB} \nabla^2 c_A \\
 \frac{\partial c_B}{\partial t} &= \mathcal{D}_{BA} \nabla^2 c_B \\
 \mathcal{D}_{AB} &= \mathcal{D}_{BA}
 \end{aligned}
 \tag{17.5}$$

Equation (17.5) is called Fick's second law of diffusion, or sometimes simply the diffusion equation. In this equation, c is the total molar concentration, c_i are the molar concentrations of the species under consideration (A, B), and \mathcal{D}_{AB} is the interdiffusion or mutual diffusion coefficient of A in B. Equation (17.5) can easily be generalized for multicomponent diffusion [25, 76]. Finally, the *intradiffusion coefficient* or tracer diffusion characterizes the diffusion of each component A or B in a uniform mixture of these components, but where the component under study, A, is chemically identical with component B but can be distinguished by some label such as an isotopic form.

The available methods for the measurement of diffusion coefficients in liquid systems have been comprehensively described [25], although there were some earlier descriptions [77, 78]. Here, we refer only the most adequate, in our judgment, to measurements in LTILs, referring previous applications, if any, to molten salts.

The diffusion coefficients depend parametrically on the thermodynamic state of the liquid and must be assigned a reference state characterized by a triplet of variables (T, P, c). In any measurement of the diffusion coefficients there are several aspects that must be considered. In ideal mixtures, for which there are no volume or enthalpy changes on mixing, when two mixtures of different composition are added together at the same temperature, some very small temperature gradients are created—the Dufour effect. Usually, these temperature heterogeneities are negligible. If the mixture is nonideal, there are volume and enthalpy changes on mixing, creating temperature heterogeneities and convective motion that have to be rendered negligible, to perform isothermal measurements. This is the case in binary mixtures of ionic liquids, mostly nonideal [79]. It follows that a primary instrument for the measurement of diffusion coefficients must satisfy several conditions. First, it is necessary to maintain a near equilibrium state by using small concentration gradients. Second, all the effects resulting from nonideal behavior must be reduced to a negligible level. Third, the bulk flow motion resulting from free convection must be minimized, as well as the Dufour effect. In addition to these conditions, and as explained in previous sections, it is necessary to have a working equation and a full set of corrections, easily calculable. Not many instruments obey these criteria, and we shall refer to some techniques that are absolute, such as the closed tube method, the Harned conductance cell,⁸ the interferometric techniques (Gouy, Rayleigh), and the Taylor dispersion method. All these methods are applicable to LTILs and the only criteria for a given choice are the required uncertainty of the measurements and the average time of duration of an experiment, as most of them, with the exception of the Taylor dispersion technique, last for more than one day for a single experiment. Table 17.6 shows the main characteristics of each of the primary methods mentioned. The close tube methods, namely, the conductance cells developed by Harned and collaborators in the 1950s [80], have been applied to aqueous salt solutions, strong and weak acids, mixed solvents, strong electrolytes, proteins, and ionic dyes; readers can find details in Reference 25. The main disadvantage of these methods, in addition to the duration of a measurement, is the limited temperature range, usually near ambient, a fact that it is not probably important for the LTILs measurements.

⁸The Harned conductance cell, used for conductimetric measurements, is in fact a close tube method.

TABLE 17.6 Existing Methods for the Measurement of Mutual Diffusion Coefficients and Their Applicability to LTILs

Method	Type	Attainable Uncertainty	Adaptability to LTILs		
			Yes	No	Average Duration of Experiments
Interferometric techniques	Primary/absolute	0.2%	✓		1–2 days
Closed tube	Primary/absolute	0.4%	✓		Days
Harned conductance	Primary/absolute	0.4–0.8%	✓		Days
Taylor dispersion	Primary/absolute	1–2%	✓		<1 hour

However, its application to molten salts has been very restricted, and with uncertainties well above those mentioned in Table 17.5. The same applies to the optical methods that seldom have been applied far from the ambient temperature, but the excellent uncertainties of the methods make them appropriate for standard reference data in a limited range of conditions. The Taylor dispersion technique, although of slightly higher uncertainty, has two great advantages over the other methods. It is very rapid and can be used, without loss of accuracy, in wide ranges of temperature and pressure. Furthermore, it has been applied already to diffusion of water + LTILs [81]. Also, as the authors have experience in the use of this method and intend to use it to measure the diffusion of water in LTILs, at low concentrations of water (in order to understand how to achieve high purity for these compounds), we shall mention it briefly.

Q6

In essence, the Taylor dispersion technique uses the velocity profile of the flow of a liquid in a cylindrical tube to enhance the dispersion of a pulse of a mixture in another one of slightly different composition, brought about only by molecular diffusion. The coupling of the flow induced dispersion with molecular diffusion results in a significant dispersion in a short time. The method was first conceived by G. I. Taylor in 1953, and its theory, that makes possible its classification as an absolute and primary method, was presented by Alizadeh et al. [82]. Figure 17.9 shows the ideal Taylor diffusion experiment.

A fluid mixture of components A and B flows in laminar flow through a straight, infinitely long, isothermal tube, of uniform circular cross section, of radius a_0 , with impermeable walls. The molar concentrations of species A and B in the flowing solution are denoted by c_{Af} and c_{Bf} and the mean velocity of the liquid mixture by \bar{u}_0 . At time $t = 0$, a sample of the liquid mixture of slightly different composition, given by c_{Ai} and c_{Bi} , with a density identical at the flowing stream (to avoid buoyancy forces), is introduced at $z = 0$ in the form of a δ pulse. The joint action of convective flow and molecular diffusion results, at a time t down the tube, in a dispersion of the pulse. The governing differential equation for the perturbation of the pulse molar concentration Δc_A is [82]

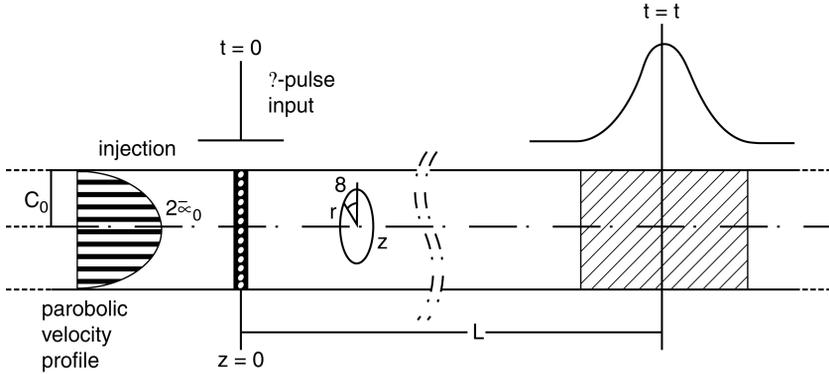


FIGURE 17.9 The ideal Taylor dispersion experiment [81].

$$\frac{1}{\mathcal{D}_{AB}} \frac{\partial(\Delta c_A)}{\partial t} = \nabla^2(\Delta c_A) - \frac{2u_0}{\mathcal{D}_{AB}} \left[1 - 2\left(\frac{r}{a_0}\right)^2 \right] \frac{\partial(\Delta c_A)}{\partial z} \quad (17.6)$$

The initial conditions for its solution are

$$\Delta c_A(r, \theta, 0, 0) = \delta(z)(c_{Ai} - c_{Af}); \quad \delta(z) \begin{cases} = 0, & z \neq 0 \\ = 1, & z = 0 \end{cases} \quad (17.7)$$

The boundary conditions are

$$\begin{aligned} \frac{\partial(\Delta c_A)}{\partial z} &= 0 & \text{at } r = a_0 \text{ for all } t \\ \Delta c_A &\rightarrow 0 & \text{as } z = \pm\infty \end{aligned} \quad (17.8)$$

This equation cannot be solved directly to obtain $\Delta c_A(z, t)$, but it can be solved for the spatial moments of the concentration distribution at a particular time. In fact, the enhanced dispersion of the pulse results in a broadening of the distribution. If we monitor the cross-sectional averaged concentration distribution at an axial position $z = L$ as a function of time, provided that

$$\frac{\mathcal{D}_{AB} t}{a_0^2} > 700 \quad \text{and} \quad u_0 > 700 \frac{\mathcal{D}_{AB}}{a_0} \quad (17.9)$$

then, with an error smaller than 0.01%, the first and the second central moments (variance) of the temporal distribution are given by [82]

$$\begin{aligned} \bar{t}_{id} &= \frac{L}{u_0} (1 + 2\xi) \\ \sigma_{id}^2 &= \left(\frac{L}{u_0}\right)^2 (8\xi^2 + 2\xi) \\ \xi &= \frac{\bar{u}_0 a_0^2}{48\mathcal{D}_{AB}L} \end{aligned} \quad (17.10)$$

If the first and the second central moments (variance) of the temporal distribution are determined at a cross section of the tube at a distance L from the injection point, the interdiffusion coefficient can be obtained from

$$\mathcal{D}_{AB} = \frac{a_0^2}{24 \bar{t}_{id}} \frac{\left[1 + 4 \frac{\sigma_{id}^2}{\bar{t}_{id}^2} \right]^{1/2} + 3}{\left[1 + 4 \frac{\sigma_{id}^2}{\bar{t}_{id}^2} \right]^{1/2} + 2 \frac{\sigma_{id}^2}{\bar{t}_{id}^2} - 1} \quad (17.11)$$

Any experimental realization of the ideal method clearly involves departures from it, and all of them have been considered by Alizadeh et al. [82]. In particular, it was found that the ideal moments have to be corrected by

$$\begin{aligned} \bar{t}_{id} &= \bar{t}_{exp} + \sum_i \delta \bar{t}_i \\ \sigma_{id}^2 &= \sigma_{exp}^2 + \sum_i \delta \bar{\sigma}_i^2 \end{aligned} \quad (17.12)$$

where \bar{t}_{exp} and σ_{exp}^2 denote the experimentally measured moments and $\delta \bar{t}_i$ and $\delta \bar{\sigma}_i^2$ are the different corrections to the ideal model [82]. They involve the finite volume of the detector, the finite volume of the injected sample, the tube connection to the detection cell, the secondary flow effects induced by the diffusion tube, the nonuniformity and the noncircularity of the tube cross section, as well as the concentration dependence of the interdiffusion coefficient, assumed constant in the ideal model. Following Alizadeh et al. [82], a suitable design can make most of these corrections negligible; the remaining ones do not contribute to more than 0.5% of the moments of the experimental curve.

The reference state of the measured diffusion coefficient is defined by the temperature and pressure of the measurement, and a composition c_{Aref} given by

$$c_{Aref} = c_{A1} + \delta c_A \quad (17.13)$$

where the correction δc_A depends on the number of moles of the species A present in the injection sample in excess of those in the flowing stream.

Alizadeh and Wakeham [83, 84] and Matos Lopes and Nieto de Castro [85] developed instruments of this type, where the detection was made by using a differential liquid refractometer, normally used in HPLC, for measurements in binary mixtures of alkanes, at atmospheric pressure and temperatures between 290 and 350 K, with an accuracy reported to be better than 1%.

Figure 17.10 shows an eluted concentration profile for an infinite dilution test of heptane in hexane, obtained by Matos Lopes et al. [86] at 24.9 °C and atmospheric pressure. The digital signal, the fitted Gaussian, and the estimates of the errors in the measured variables \bar{t}_{exp} and σ_{exp} all show perfect agreement between the model and the experiment. The later instrument was then applied to study more complex systems like diffusion in homogeneous and micellar solutions [87], and near the consolute point of a binary mixture [88]. This last application was fundamental support for

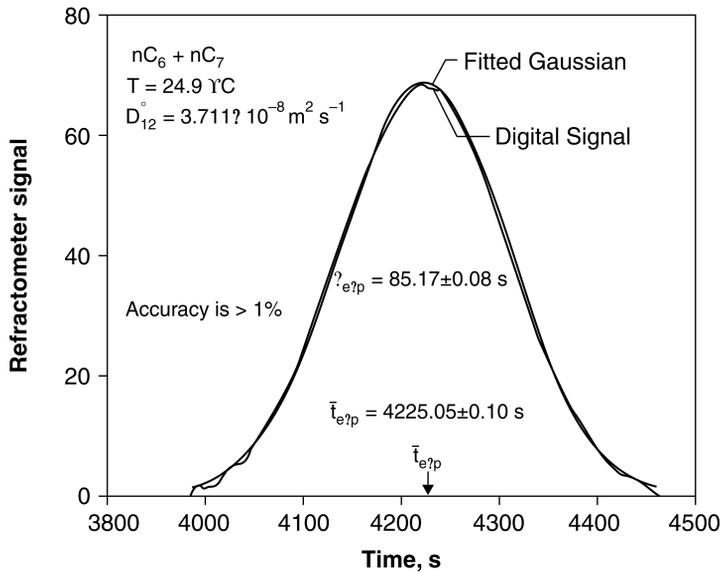


FIGURE 17.10 The eluted concentration profile for an infinite dilution test of heptane in hexane at 24.9 °C. The digital signal is compared with the fitted Gaussian. Estimates of the errors in the principal variables \bar{t}_{exp} and σ_{exp} are also shown [85].

previous results obtained from dynamic light scattering and the theory of the critical enhancement of diffusivity, where the diffusivity decreases upon approaching the critical temperature, eventually vanishing to zero (Fig. 17.11). This result seems very important for ionic liquid applications, namely, when used as a solvent or as a reaction media in supercritical conditions or near immiscibility. Since these measurements, the technique has been applied to several systems, showing its versatility in some applications to wide ranges of temperature and pressure [89]. Many other authors have applied the method since then, and details can be found in Reference 89. It can also be applied to study reference systems, such as the mixture $\text{H}_2\text{O} + \text{D}_2\text{O}$ [90]. The results can be applied to study the structure of liquid mixtures, including specific interactions, short-range anisotropy, and packing, as demonstrated by Oliveira et al. [91] for the effect of branching in hexane in the binary diffusion coefficients.

As mentioned before, this technique has been applied with success to alkyliimidazolium tetrafluoroborates and hexafluorophosphates in water at room temperature [81] at infinite dilution of the LTILs, the system previously tested with NaCl, with an accuracy of 0.8%. The liquids studied were $[\text{C}_n\text{mim}][\text{BF}_4]$ and $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 2, 4, 6, \text{ or } 8$). Figure 17.12 shows the dependence of the infinite dilution diffusivity as a function of the formula weight for the two series studied. It is interesting to note that the values obtained for the infinite dilution diffusivity in water of $[\text{C}_6\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ are similar to the same quantity for the infinite dilution of heptane in dodecane [85] ($\sim 1.2 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$).

To study the influence of water on the purity of the LTILs, the measurements of the diffusivity have to be performed near infinite dilution of water in the LTILs.

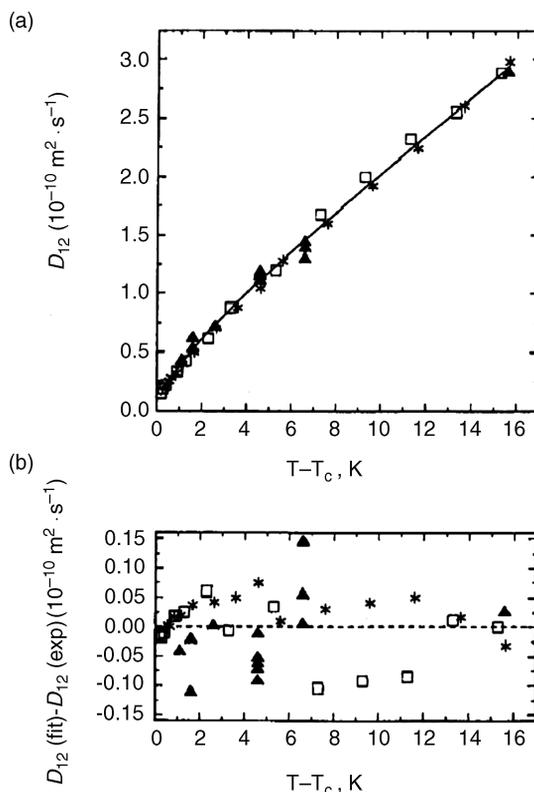


FIGURE 17.11 (a) Mutual diffusivity \mathcal{D}_{AB} of a mixture of hexane and nitrobenzene at the critical composition as a function of $T - T_c$. The curve represents the values calculated using the theory of critical dynamics [87]. (b) Difference between experimental and calculated diffusivities. \blacktriangle , cited work; \square , Reference 92; $*$, Reference 93.

17.4 CONCLUSION

Low temperature ionic liquids with strong charge dislocation, polarity, and weak to moderate electrical conduction raise some problems regarding the accurate measurement of thermophysical properties, namely, transport properties. The methods of measurement have to be adapted to these types of liquids. This is indeed true for measuring the thermal conductivity, viscosity, electrical conductivity, and dielectric constant. For these properties, the fact that the liquid is ionic and therefore electrically conducting, and usually highly viscous, when subjected to thermal gradients, stresses, and electrical fields, generates several phenomena like electric double layers, viscous heating dissipation, and the need for sensor electrical isolation that make experiments difficult to perform with high accuracy, even for temperatures around room temperature. New cells, new cable screenings, new signal analysis, and so on have to be envisaged. New reference liquids for property measurement, necessary for end-user relative methods, have to be devised and internationally accepted.

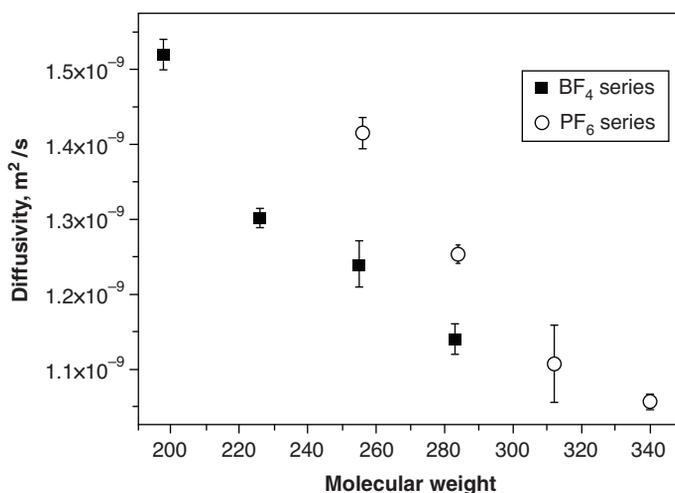


FIGURE 17.12 The variation of the diffusion coefficients of alkyimidazolium tetrafluoroborates and hexafluorophosphates in water with their formula weights [80]. The liquids studied were $[C_n\text{mim}][\text{BF}_4]$ and $[C_n\text{mim}][\text{PF}_6]$ ($n = 2, 4, 6, \text{ or } 8$).

An international effort, which can strengthen the first efforts to produce new and high quality property data (IUPAC Project, Ken Marsh—coordinator) has to be supported. Among others, the properties to be measured (around room temperature to temperatures up to thermal degradation) are thermal conductivity, heat capacity, viscosity, electrical conductivity, electrical permittivity, surface tension, density, and diffusion of water in ionic liquids. These will support the key data for the necessary changes in existing chemical processes or for the design of new processes, based on green or sustainable chemistry. Our research group is prepared to contribute to this effort by measuring most of these properties in selected ionic liquids.

Finally, the levels of impurities in different LTILs, hydrophilic or not, have to be measured, if the data uncertainty is required to be 3% or better. The fact that the water absorption or dissolution is a time-dominated process at these low concentrations restricts the use of samples in industry for property-sensitive processes, requiring special care in production and quality control.

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