How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-based Ionic Liquid by Microwave Dielectric Spectroscopy

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In a pilot study of the dielectric constant of room-temperature ionic liquids, we use dielectric spectroscopy in the megahertz/gigahertz regime to determine the complex dielectric function of five 1-alkyl-3-methylimidazolium salts, from which the static dielectric constant ϵ is obtained by zero-frequency extrapolation. The results classify the salts as moderately polar solvents. The observed ϵ-values at 298.15 K fall between 15.2 and 8.8, and ϵ decreases with increasing chain length of the alkyl residue of the cation. The anion sequence is trifluoromethylsulfonate > tetrafluoroborate ≈ tetrafluorophosphate. The results indicate markedly lower polarities than found by spectroscopy with polarity-sensitive solvatochromic dyes.

Introduction

The past decade has seen a plethora of research on imidazolium-based room-temperature ionic liquids (ILs) as environmentally benign solvents in diverse applications, for example in chemical synthesis, catalysis, separation technology, or electrochemistry.[1] Much effort to date has focused on the characterization of the bulk physical properties of ILs and their correlation with molecular properties. In the present study we report data on the static dielectric constant ϵ of prototypical ILs.

The dielectric constant is a key parameter for modeling solvent behavior because many approaches rely on dielectric continuum models for the solvent. In correlation with molecular properties widely used in chemistry and chemical engineering, the dielectric constant is an important measure for the polarity of a solvent. Conventional techniques for measuring static dielectric constants of ILs fail, however, because the samples are largely short-circuited by the high electrical conductance. The question "How polar are ionic liquids?" has therefore given rise to efforts for establishing alternative experimental polarity probes, for example based on solvatochromic shifts and fluorescence of probe dyes,[2] partitioning of solutes in water−IL bilayers,[3] gas chromatography with ILs as stationary phases,[4] or solvent effects on chemical reactions.[5] Polarity is, however, not rigorously defined, and polarity scales depend on the experimental method used. In part, reported polarities of ILs differ substantially.

The purpose of this study is two-fold: First, we aim at demonstrating that the dielectric constant of ILs can be determined experimentally by microwave dielectric spectroscopy, using methods successfully applied to electrolyte solutions[6] and ionic glasses,[7] and recently extended by us to conductive molten ethylammonium nitrate.[8] Second, we will illustrate the method by reporting dielectric constant data for five prototypical ILs. These results will establish the general order of magnitude of this quantity and will indicate trends for the cation and anion dependence. We emphasize that this paper does not aim at discussing the molecular mechanisms that generate the dielectric polarization. Such an analysis inevitably requires an understanding of the highly complex and multimodal nature of the dielectric spectra up to the optical regime and will be performed in future work.[9]

Method

We probe the frequency-dependent complex dielectric function $\tilde{\epsilon}(\nu)$ between 1 MHz and 20 GHz by coaxial reflectance techniques described elsewhere.[10] The experiments provide information on the real part $\epsilon'(\nu)$ (dielectric dispersion) and imaginary part $\epsilon''(\nu)$ (dielectric absorption or loss) of $\tilde{\epsilon}(\nu)$[11]

$$\tilde{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) = \epsilon_\infty + \Delta\tilde{\epsilon}(\nu) + \sigma/i2\pi\nu\epsilon_0 \quad (i^2 = -1) \tag{1}$$

where $\Delta\tilde{\epsilon}(\nu)$ stands for frequency-dependent processes in the MHz/GHz regime. We focus here on the dispersion curve $\epsilon'(\nu)$. In addition to the frequency-dependent part $\Delta\epsilon'(\nu)$, there is a high-frequency contribution ϵ_∞ to the dispersion caused by nuclear and electronic displacement polarizations in the infrared and optical regimes.[11] In practice, fits of the dispersion curve up to 20 GHz provide, however, ϵ_∞ values that also absorb contributions from processes in the far-infrared regime, known to be present from terahertz spetroscopy.[12] The static dielectric constant follows from the zero-frequency intercept:[11]

$$\epsilon \equiv \epsilon_\infty + \lim_{\nu \to 0}\Delta\epsilon'(\nu) \tag{2}$$

Our experiments also provide the imaginary part $\Delta\epsilon''(\nu)$ of the complex permittivity, which is rigorously related to the real part $\Delta\epsilon'(\nu)$ by the Kramers−Kronig relation and therefore comprises the same information as $\Delta\epsilon'(\nu)$.[11] The absorption

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TABLE 1: Static Dielectric Constants of Imidazolium-based Ionic Liquids at 298.15 K

compound	ϵ
EtMeIm$^+$ Tf$^-$	15.2 ± 0.3
EtMeIm$^+$ BF$_4^-$	12.8 ± 0.6
BuMeIm$^+$ BF$_4^-$	11.7 ± 0.6
BuMeIm$^+$ PF$_6^-$	11.4 ± 0.6
HexMeIm$^+$ PF$_6^-$	8.9 ± 0.9

spectrum is, however, superposed by a diverging low-frequency response proportional to the static (d.c.) conductivity σ of the sample (cf. the last term in eq 1, where ϵ_0 is the permittivity of the vacuum). Because the conductance term dominates over large parts of the MHz/GHz spectrum, the accurate characterization of $\Delta\epsilon''(\nu)$ is difficult. We therefore focused on the dispersion curve, but we ensured that all data were consistent with the results for $\Delta\epsilon''(\nu)$.

The success of our experiments required to overcome two major problems. First, low-frequency processes at the interface between the electrically conducting liquid and the sample cell gave rise to apparatus-specific polarizations. Second, coaxial techniques require calibration with accurate standards, preferably with dielectric behavior and electrical conductivity similar to the samples under test. The available standards[13] do not satisfy these conditions. Inadequate calibrations gave rise to distortions in the spectra, which sometimes were highly reproducible, thus mimicking additional modes. We could identify and eliminate these artifacts by careful comparison of results obtained with several available standards[13] and by experiments with specimen cells of different geometries. These variations of experimental conditions convinced us that systematic errors were unlikely to be unnoticed, at least down to 10 MHz.

Results and Discussion

We consider five 1-alkyl-3-methylimidazolium salts of the type RMeIm$^+$ X$^-$ listed in Table 1. R stands for ethyl (Et), *n*-butyl (Bu), and *n*-hexyl (Hex) residues, X$^-$ for tetrafluoroborate (BF$_4^-$), hexafluorophosphate (PF$_6^-$), and trifluoromethylsulfonate (triflate, Tf$^-$). The triflate was purchased from Fluka (Basel, Switzerland), the other salts from Solvent-Innovation (Köln, Germany). The purities quoted by the manufacturers were > 98% for the triflate and the tetrafluoroborates and > 99% for the hexafluorophosphates. The quoted water content of the purchased samples was typically about 300 ppm. Before use the salts were dried for 48 h at 70 °C and 10^{-5} bar.

For all salts, the spectra were recorded from 1 MHz to 20 GHz, but accurate data could be obtained over only part of this range. Typically, three regions were identified. Between 200 MHz and 20 GHz highly accurate spectra were obtained. Between 10 and 200 MHz the scatter of the data increased rapidly with decreasing frequency, and eventually near 10 MHz no meaningful data could be extracted due to calibration-specific and cell-specific effects that could not be suitably corrected for. Except for HexMeIm$^+$ PF$_6^-$, the major parts of the dispersion regimes were, however, located above 200 MHz, and the less accurate data below 200 MHz were omitted in spectral parametrization. It is, however, crucial to note that, albeit omitted in the final fits, the low-frequency data safely excluded the presence of additional modes, at least down to 10 MHz. Figure 1 shows the dispersion curve of EtMeIm$^+$ Tf$^-$ at 298.15 K as used in the final parametrization. The zero-frequency intercept of the dispersion curve defines the static dielectric constant.

For equating our extrapolated values with the real static dielectric constant, we have to ensure that there are no undetected modes below 10 MHz. For highly conductive
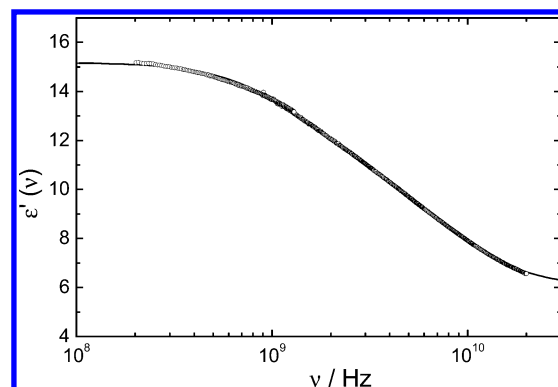
Figure 1. Dielectric dispersion spectrum of EtMeIm$^+$ Tf$^-$ at 298.15 K. The static dielectric constant is given by the zero-frequency intercept of the curve. The solid line shows the fitted curve.

systems this cannot be proved by dielectric spectroscopy itself. There is, however, a series of arguments that such processes are very unlikely. The rationale is that for ILs of the given viscosities, up to 500 cP say, all molecular translational and reorientational processes that may drive dielectric relaxation will occur at the nanosecond and subnanosecond time scales, as established by hydrodynamic arguments, MD simulations of translational and rotational dynamics,[14] and by several spectroscopic probes of dynamical processes such as Stokes shift spectroscopy of probe dyes[15] and magnetic relaxation dispersion experiments for cation reorientation.[16] Any mode below 10 MHz would come as a surprise because it would indicate a hitherto unknown relaxation mechanism, not present in nonliquids, electrolyte solutions, or ionic glasses. Thus, there is convincing evidence that our extrapolation indeed provides the static dielectric constant. This is, of course, not true for a recent attempt[12] to extrapolate the "effective dielectric constant" of EtMeIm$^+$ Tf$^-$ from terahertz spectroscopic data (200 GHz < ν < 1 THz).

In detail, we fitted the data above 200 MHz to a series of relaxation models, e.g., compiled in ref 8. A simple Debye model, as adequate for many dipolar fluids,[11] was insufficient. Good fits were obtained for a model comprising two Debye-type modes. Fits of comparable quality were also obtained for the Cole−Davidson distribution of relaxation times.[17] The extrapolated values of ϵ differed only marginally. Models with a larger number of fit parameters, e.g., three Debye terms, involved too many degrees of freedom for deriving unambiguous fit parameters but resulted in practically the same zero-frequency intercepts as the models considered here. Table 1 compiles the resulting values of ϵ at 298.15 K.

The uncertainties quoted in Table 1 are based on the quality of the fits and the reproducibility of ϵ in experiments with different calibrations, different probe geometries, and different batches of the substances. The high accuracy assigned to EtMeIm$^+$ Tf$^-$ reflects the fact that this salt was applied by us for optimizing the experimental conditions. The low accuracy for HexMeIm$^+$ PF$_6^-$ is mainly due to the fact that part of the spectrum falls below 200 MHz. Practically all spurious and systematic errors identified by us in the course of our experiments led to an apparent increase of ϵ. Noting the typical halide content of the order of 500 ppm (mainly chloride) and the residual water content after drying (<300 ppm), we carefully examined the extent to which these impurities could affect the results. We therefore deliberately added water up to 1 vol-% and NaCl up to 500 ppm to the samples. Although the conductance increased by up to 3%, no systematic trends were observed in the dielectric constant. Typically, it needed 0.5−1

vol-% of water to generate an increase beyond the error limits given in Table 1. The weak effect is in agreement with predictions by simple mixing rules[11] which, to a first approximation, interpolate the dielectric constant linearly between the two values of the pure liquids at a volume fraction basis. These observations do not indicate a particularly weak sensivity of ϵ to impurities, but mainly reflect the fact that measurements with highly conductive systems are of limited accuracy.

Our results classify ILs as media of moderate polarity. In the cases under test, the dielectric constants fall in the range between $8.8 \leq \epsilon \leq 15.2$. ϵ decreases with increasing chain length of the alkyl residue R of the 1-alyl-3-methylamimidazolium salt. The observed anion sequence is $Tf^- > BF_4^- \approx PF_6^-$.

Most reported polarity studies of ILs rely on polarity-sensitive dyes and fluorescence probes.[2] Despite some discrepant results obtained with different probes,[2f] some general trends are obvious. Most probes assign to ILs a higher polarity than observed here. Taking the work of Reichardt[2a] and Aki et al.[2c] as representative examples, polarities of ILs are expected to be close to those of short-chain alcohols such as methanol ($\epsilon = 32.5$). Our results reveal more moderate polarities, for example, corresponding to those of alcohols of intermediate chain length such as n-pentanol ($\epsilon = 15.1$) and n-octanol ($\epsilon = 8.8$). Moreover, it follows from most studies that the polarity mainly depends on the nature of the cation.[2c] Our results show that ϵ depends markedly on the anion.

Conclusions

When selecting a solvent for applications, an important quantity is its polarity. There lacks, however, a rigorous definition of this quantity which, as is commonly understood, depends on a complex mix of electrostatic and specific interactions. Thus, polarity scales are always empirically defined. In molecular liquids the static dielectric constant is thought to provide a measure of the polarity which, unlike some other probes, is well founded in rigorous molecular theory.[11]

Our experiments show that, by exploiting the definition of ϵ as the zero-frequency limit of the frequency-dependent dielectric dispersion, dielectric constants can also be measured for electrically conductive ILs. In our experiments, we have determined the dielectric constants of five prototypical ILs. While the values have uncertainties larger than those measured by conventional techniques for nonionic fluids, there are no basic limitations of our technique that would prevent the future design of more accurate experiments. At present, the major obstacle is the lack of adequate calibration standards.

Our results classify ILs as solvents of moderate polarity. They also show that ϵ can be tuned over an appreciable range by variation of both the cation and anion. Our data indicate a polarity that is markedly lower than that obtained with most other probes. However, the well-established scenarios for describing dipolar interactions in molecular liquids[11] are not easily transferred to ILs because the net charges of the ions create a fundamentally different environment with partial charge-ordering and screening of dipole–dipole interactions by the sea of surrounding ions. The presence of charged species adds new degrees of freedom in the mix of interactions. In this case, the concept of polarity may even require a careful rethinking of the fundamental nature of solvation.[18]

Finally, as noted at the very outset, we do not intend here to discuss the dielectric spectrum itself. Based on experience with nonionic fluids, one would assign the observed modes to reorientational motions of dipolar ions and/or dipolar ion pairs. Moreover, there are additional relaxation mechanisms in our charged systems because collective translational motions of ions may also drive relaxation.[8] This multitude of scenarios and the multimodal nature of the spectrum with additional processes in the THz regime will render any interpretation highly speculative. We will postpone detailed discussion of these aspects to a future study.[9]

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