

## COMMENTS

**Comment on “How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-based Ionic Liquid by Microwave Dielectric Spectroscopy”**Frank V. Bright<sup>\*,†</sup> and Gary A. Baker<sup>‡</sup>

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Wakai et al.<sup>1</sup> recently reported the determination of the static dielectric constant  $\epsilon$  for five prototypical imidazolium-based room-temperature ionic liquids (RTILs) using microwave dielectric spectroscopy (MDS) in the MHz/GHz regime. As they correctly point out, direct conventional measurements of  $\epsilon$  require a nonconducting medium and thus fail for RTILs, which are essentially short-circuited by the high electrical conductance intrinsic to this novel class of solvent. In an alternative method, a zero-frequency extrapolation routine was performed on the real part  $\epsilon'(v)$  of the frequency-dependent complex dielectric function for data collected between 200 MHz and 20 GHz. The zero-frequency intercept of the dielectric dispersion spectrum for each solvent provided a reproducible estimate of  $\epsilon$  which ranged from 8.9 to 15.2 for the RTILs investigated. We agree that this work makes a significant contribution to our collective understanding and classification of RTILs as solvents. Unfortunately, there are a couple of important omissions we seek to clarify in this commentary.

In particular, the authors do not cite relevant prior work in which  $\epsilon$  was estimated using polarity-sensitive fluorescent molecular probes.<sup>2,3</sup> In the first example, Bonhôte et al.<sup>2</sup> suggested an upper limit near 10 for 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide based on the emission profile of 1-pyrenecarboxaldehyde. Additionally, we have shown earlier in this journal that a dual solvatochromic probe approach may offer an alternative method for the indirect estimation of  $\epsilon$ .<sup>3</sup> Specifically, it is well established that the pyrene emission band ratio ( $I_1/I_3$ ) is linearly related to the dielectric cross term,  $f_1(\epsilon, n^2)$ , for a wide range of conventional solvents. Similarly, the Stokes shift (SS) for the probe PRODAN is a linear function of the solvent's orientational polarizability,  $f_2(\epsilon, n^2)$ . For the purpose of our argument here, the exact forms of  $f_1(\epsilon, n^2)$  and  $f_2(\epsilon, n^2)$  are not essential, although both contain as a term Kirkwood's function  $F(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$ . This led us to the notion that, by interpolation of the values of  $f_1(\epsilon, n^2)$  and  $f_2(\epsilon, n^2)$  from experimental measures of  $I_1/I_3$  and SS, respectively, relative to a host of “normal” organic molecular liquids, one can simultaneously solve these two expressions for  $\epsilon$  and  $n$ . The result of this exercise gave a static dielectric constant of  $\epsilon = 11.4 \pm 1.0$  for the RTIL 1-butyl-3-methylimidazolium

hexafluorophosphate, [bmim][PF<sub>6</sub>], at 293 K.<sup>3</sup> This result is in remarkable agreement with the quantity  $11.4 \pm 0.6$  determined via MDS at 298 K.<sup>1</sup> So, noting that permittivity measurements are unavailable by *direct* measurement, taken together these reports provide some measure of mutual validation on the reliability of these two disparate approaches.<sup>1,3</sup> We note that a paper by Pierini and co-workers submitted prior to ref 1 has recently appeared that evaluates  $\epsilon$  on the basis of the keto–enol tautomeric equilibrium constant of 2-nitrocyclohexanone measured by UV–visible and <sup>1</sup>H NMR spectroscopy.<sup>4</sup> Although the mean uncertainty in  $\epsilon$  given was rather large in this report (ca. 30%), a reasonably consistent value was determined for [bmim][PF<sub>6</sub>] at 298 K ( $\epsilon = 10.0 \pm 1.5$ ).

As suggested in ref 1 and highlighted by us and several other researchers elsewhere, the difficulty of producing a single parameter capable of adequately and reliably describing solvent polarity is considerable. We further suggest that  $\epsilon$  is, in this regard, likely no more definitive a measure of overall polarity than is Reichardt's commonly used  $E_T(30)$  index, for example. Furthermore, the authors of the current paper in their abstract conclude, “The results indicate markedly lower polarities than found by spectroscopy with polarity-sensitive solvatochromic dyes.”<sup>1</sup> Of course, in view of the fact that we arrive at identical values for  $\epsilon$  within the error limits quoted on the basis of our particular approaches, this cannot be entirely the case. This being said, there are certainly legitimate limitations and concerns associated with the selection of a particular probe for estimating RTIL physicochemical properties such as  $\epsilon$ . Many fluorescent probes, and perhaps even most, will be completely unsuited for this task. Moreover, the frequency dependence of permittivity is not accessible from such measurements. On the other hand, we envisage growth in the application of ancillary methods based on solvatochromic probe responses, particularly given that the specialized instrumentation and expertise required for techniques such as MDS are less widely available. In addition, probe-based methods can often reveal key information concerning solute/solvent and solvent/solvent interactions and dynamics within RTILs that are not available from MDS; hydrogen-bond strength, and microviscosity, for example.<sup>5</sup>

From a practical viewpoint, single-parameter spectroscopic measures of solvent polarity are quickly and conveniently obtained; however, a growing number of reports have questioned their validity. This has been particularly true of fluorescent molecular probing of RTILs. In response, we offer that although a single probe cannot experience the diversity of interactions that the whole range of solvents can offer, most often any confusion or ambiguity in their use arises from an inadequate understanding of precisely what solvent features the probe is actually reporting on rather than any true limitation of this approach per se. Thus, while choice of probe for one's purpose is clearly important, so too is the correct interpretation of the exact spectroscopic response and its origin for a given probe. Undoubtedly, in our experience in this area, we have learned that the three primary sources of misinterpretation found in the literature reflect a failure to account for or fully appreciate one or more of the three following facts. (i) Individual probes will favor specific probe/solvent interactions. (ii) Given the magni-

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tude of the viscosities within typical RTILs, say 20 to over 300 cP, solvent relaxation/reconfiguration in the excited-state probe's cybotactic region may frequently be incomplete prior to emission of a photon; most probes have a radiative decay rate between  $10^7$  and  $10^9$  s<sup>-1</sup>. A case in point is the lower-than-expected value for  $\epsilon$  determined by Bonhôte et al.,<sup>2</sup> a result almost certainly originating in fluorescence from a nonequilibrium solvation state of the probe studied. Finally, (iii) the composition of the solvent in the vicinity of the probe in RTILs may deviate significantly from that of the bulk (i.e., preferential solvation) and, to further complicate issues, many solvents do not mix ideally even in the absence of solutes.<sup>5</sup> A fairly comprehensive discussion of these concepts as they apply to RTIL research will be reported elsewhere (Baker et al., in preparation). In closing, we note that "hidden" modes below the 10 MHz window in the dielectric dispersion spectra of Wakai et al.<sup>1</sup> cannot be probed directly by dielectric spectroscopy itself, and the rationale for the exclusion of such processes comes instead from fluorescence-based solvent relaxation results established earlier by a number of groups. Overall, while a more direct and elegant technique

such as MDS may be clearly preferred when available, there is ample support for our assertion that fluorescence spectroscopy will also continue to contribute significantly to a molecular-level view of solvation within RTILs both as a complement to other methods and in acquiring information not otherwise available. In either case, we note that the determination of reliable and consistent physicochemical parameters depends crucially on the preparation of samples of known purity, an aspect that deserves further scrutiny.

## References and Notes

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