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Static Relative Dielectric Permittivities of Ionic Liquids at 25 °C

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ABSTRACT: For understanding solvation by ionic liquids, it is mandatory to characterize their static relative dielectric permittivities ε ("static dielectric constants"). Exploiting the definition of ε in terms of the zero-frequency limit of the frequency-dependent dielectric dispersion curve, the static dielectric constant of an electrically conducting liquid can be extrapolated from dielectric relaxation spectra in the microwave regime. On the basis of this method, we report dielectric constants of 42 ionic liquids at 25 °C.

INTRODUCTION

The static relative dielectric permittivity ε of a solvent,[1] usually called "static dielectric constant", is a key property for understanding its solvation capability and forms an important input parameter of many modelings of solvation processes. The past decade has seen the advent of ionic liquids (ILs)[2]—organic salts which are liquid at or near room temperature—as innovative solvents which can revolutionize chemical methodologies. For assessing solvation by ILs it is mandatory to characterize and understand their static dielectric constants.[3−5]

The concept of the static dielectric constant of an electrically conducting liquid is subtle. Capacitance methods for measuring ε fail because the sample cell is short-circuited by the electrical conductance of the sample. In contrast to a widely held opinion[6] the static dielectric constant of a conducting liquid is by no means ill-defined or infinite. Dielectric theory defines ε as the zero-frequency limit ($\nu \rightarrow 0$) of the dielectric dispersion curve $\varepsilon'(\nu)$, which forms the real part of the frequency-dependent complex dielectric permittivity $\varepsilon^*(\nu)$.[1,7] For ILs of low viscosity, up to 500 mPa·s (500 cP) say, the relevant part of $\varepsilon'(\nu)$ falls into the MHz/GHz regime covered by microwave dielectric relaxation spectroscopy (DRS).[8−10] For a long time this method has been used for determining static dielectric constants of highly conducting electrolyte solutions.[11]

Because of the huge number of possible cation−anion combinations,[12] it is impossible to determine the static dielectric constants of even a small fraction of the ILs of interest. The present study aims at establishing a representative database, which elucidates the most important trends imposed by cation and anion variation. For this purpose we have measured the static dielectric constants of 42 ILs at 25 °C. Because progress in understanding dielectric processes in ILs suggests a modification of the dielectric model used in our data evaluation,[13,14] we also revise some data published earlier.

METHODS

Materials. Table 1 documents sources of the ILs used. 1-*H*-3-methylimidazolium chloride (**1**) and the corresponding bromide (**2**) were synthesized according to a modified literature procedure,[15] where single equivalents of HCl or HBr were employed to yield 1:1 salts. The synthesis of some ILs followed literature procedures specified in Table 1: ILs comprising the bis(trifluoromethylsulfonyl)imide anion ($[NTf_2]^-$),[16] 1-alkyl-2,3,4,5-tetramethylimidazolium salts,[17] ethylammonium nitrate,[8] and OH-functionalized ILs.[18] All other salts were purchased from Iolitec (Heilbronn, Germany) or Solvent-Innovation (Cologne, Germany), as marked in Table 1.

Most ILs were dried up to 48 h at 60 °C and 1 mbar to achieve a weight fraction of water of less than 10^{-4}, as determined by Karl Fischer titration. The Cl^- content, which is of concern in many applications, is uncritical in our experiments up to at least a weight fraction of 10^{-3} because Cl^- is dielectrically inactive and affects dielectric properties only indirectly via its effect on the IL structure.

Hydrolysis of $[PF_6]^-$ and $[BF_4]^-$ ions[19] and decomposition of ammonium-based protic ILs into amines and acids[20] were of special concern to us. We dried the relevant ILs for up to one week at 25 °C and 1 mbar and surveyed decomposition by ^1H and ^{13}C NMR spectroscopy. Because drying at elevated temperatures enhanced decomposition, impurities and water were tolerated in these cases up to weight fractions of 10^{-3} each. Measurements of aqueous mixtures of the formates (**32**) and (**37**) over the complete composition range[21] show that at high IL concentrations, for example at weight fractions above 0.75, the static dielectric constant is rather insensitive to the water content.

Dielectric Relaxation Spectroscopy. Our coaxial method[9] is able to probe the complex dielectric function $\varepsilon^*(\nu)$ in the frequency range 0.3 MHz $\leq \nu \leq$ 20 GHz. The method requires three-point calibration at each frequency, made with an open circuit, a short circuit, and water or benzonitrile[22] as a calibration

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Table 1. Static Relative Dielectric Permittivities (Dielectric Constants) of Ionic Liquids (ILs) at 25 °C

no.	IL	ε
	Methylimidazolium-Based ILs	
1	1-*H*-3-methylimidazolium chloride[a]	13.8 ± 1.0
2	1-*H*-3-methylimidazolium bromide[a]	16.6 ± 1.2
3	1,3-dimethylimidazolium dimethylphosphate[b]	29.6 ± 1.5
4	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[c]	12.0 ± 0.4[h]
5	1-ethyl-3-methylimidazolium trifluoromethanesulfonate[d]	16.5 ± 0.5
6	1-ethyl-3-methylimidazolium diethylphosphate[b]	16.9 ± 0.8
7	1-ethyl-3-methylimidazolium hydrogensulfate[d]	18.4 ± 0.8
8	1-ethyl-3-methylimidazolium butylsulfate[d]	30.0 ± 1.5
9	1-ethyl-3-methylimidazolium ethylsulfate[d]	35.0 ± 1.5
10	1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[c]	13.3 ± 0.4[h]
11	1-butyl-3-methylimidazolium trifluoromethanesulfonate[d]	12.9 ± 0.5
12	1-butyl-3-methylimidazolium thiocyanate[d]	13.7 ± 0.8
13	1-butyl-3-methylimidazolium tetrafluoroborate[d]	13.9 ± 0.4
14	1-butyl-3-methylimidazolium hexafluorophosphate[d]	14.0 ± 0.7
15	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[d]	14.0 ± 0.5[h]
16	1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[c]	15.0 ± 0.5[h]
17	1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide[c]	12.8 ± 0.4
18	1-butyl-2,3-dimethylimidazolium hexafluorophosphate[d]	9.4 ± 1.0
19	1-butyl-2,3-dimethylimidazolium tetrafluoroborate[d]	13.3 ± 0.6
20	1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide[d]	14.0 ± 0.8
21	1-butyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate[e]	12.0 ± 0.6
22	1-butyl-2,3,4,4-tetramethylimidazolium bis(trifluoromethylsulfonyl)imide[e]	15.0 ± 0.8
	Aprotic ILs with Other Cations	
23	1-butylpyridinium bis(trifluoromethylsulfonyl)imide[c]	15.3 ± 0.5[i]
24	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide[c]	14.7 ± 0.5[i]
25	1-butyl-1-methylpyrrolidinium dicyanamide[d]	18.0 ± 0.8
26	1-pentyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide[d]	12.5 ± 0.6
27	butyltrimethylammonium bis(trifluoromethylsulfonyl)imide[d]	15.7 ± 1.0[i]
28	pentyltriethylammonium bis(trifluoromethylsulfonyl)imide[c]	12.5 ± 0.7
29	triethylsulfonium bis(trifluoromethylsulfonyl)imide[d]	15.8 ± 0.8[i]
	Ammonium and Pyrrolidinium-Based Protic ILs	
30	methylammonium formate[d]	41.0 ± 1.5[j]
31	ethylammonium nitrate[f]	26.3 ± 0.5[k]
32	ethylammonium formate[d]	31.5 ± 1.5[j]
33	butylammonium formate[d]	23.0 ± 1.0[j]
34	1-methylpyrrolidinium formate[d]	23.1 ± 1.0[j]
	ILs with OH-Functionalized Cations	
35	(2-hydroxyethyl)ammonium acetate[g]	58.3 ± 2.5
36	(2-hydroxyethyl)ammonium nitrate[g]	60.9 ± 2.0
37	(2-hydroxyethyl)ammonium formate[g]	61.0 ± 2.0[j]
38	(2-hydroxyethyl)ammoniu lactate[g]	85.6 ± 3.0
39	tris(2-hydroxyethyl)ammonium aetate[g]	31.0 ± 1.5
40	tris(2-hydroxyethyl)ammonium lactate[g]	59.7 ± 3.0
41	1-(2-hydroxyethyl)-3-methylimidazolium tetrafluorborate[d]	23.3 ± 1.0
42	1-ethyl-(2-hydroxyethyl)pyridinium ethylsulfate[d]	35.0 ± 2.0

[a] Synthesized according to a modified literature procedure.[15] [b] Sample purchased from Solvent-Innovation (Cologne, Germany). [c] Synthesized as described by us in ref 16. [d] Sample purchased from Iolitec (Heilbronn, Germany). [e] Synthesized according to a literature procedure.[17] [f] Synthesized as described by us in ref 8. [g] Synthesized according to a literature procedure.[18] [h] Re-evaluation of dielectric spectra published in ref 9. [i] Re-evaluation of dielectric spectra published in ref 26. [j] Re-evaluation of dielectric spectra underlying the dielectric constants published in ref 21. [k] Re-evaluation of dielectric spectra published in ref 8.

standard. Several spectra were recorded for each sample and were averaged.

$\varepsilon^*(\nu)$ can be written as[1,7]

$$\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) = \varepsilon_\infty + \Delta\varepsilon'(\nu) - (i\Delta\varepsilon''(\nu) + \kappa_{dc}/2\pi\nu\varepsilon_0) \quad (i^2 = -1) \tag{1}$$

The real part $\varepsilon'(\nu)$ is denoted as dielectric dispersion, the imaginary part $\varepsilon''(\nu)$ as dielectric loss. The property of key interest is the frequency-dependent dielectric dispersion $\varepsilon'(\nu)$ which reflects the ability of the sample to follow the oscillating electric field. $\varepsilon'(\nu)$ comprises a nonrelaxing high-frequency contribution, ε_∞, mainly resulting from the molecular polarizability of the ions, and a contribution, $\Delta\varepsilon'(\nu)$, which can involve several modes for to relaxation processes in the MHz-to-THz regime. The static dielectric constant ε is defined as the zero-frequency limit of $\varepsilon'(\nu)$.

By contrast to systems of uncharged species, where relaxation is only driven by orientational motions of the molecular dipoles, translational motions of charged species contribute to dielectric relaxation as well. In ILs with dipolar ions dielectric relaxation is therefore partly dipolar and partly ionic. As a consequence the static dielectric constant of an IL has dipolar as well as ionic contributions, which cannot be separated experimentally.

Our experiments also provide the dielectric loss, $\varepsilon''(\nu)$ which, in principle, yields the same information as $\varepsilon'(\nu)$.[1] $\Delta\varepsilon''(\nu)$ reflects absorption of electromagnetic radiation by the sample. Besides the relaxation contribution $\Delta\varepsilon''(\nu)$ of interest here, $\varepsilon''(\nu)$ exhibits a divergent low-frequency response ("Ohmic loss") of the form $\kappa_{dc}/2\pi\nu\varepsilon_0$ caused by the direct current electrical conductivity κ_{dc} of the sample. ε_0 is the dielectric permittivity of the vacuum. In highly conducting systems the $1/\nu$ divergence of the Ohmic loss renders the low-frequency part $\Delta\varepsilon''(\nu)$ of interest a small fraction of the measured loss curve $\varepsilon''(\nu)$. For determining ε we therefore resorted to the more accurate dispersion curve $\varepsilon'(\nu)$. We confirmed, however, that in each case, the results for dispersion and loss were consistent with one another.

For illustration, Figure 1 shows the measured dispersion curve, $\varepsilon'(\nu)$, of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (**5**) at 25 °C. Near 200 MHz $\varepsilon'(\nu)$ approaches a low-frequency plateau, signaling static conditions. Below 200 MHz $\varepsilon'(\nu)$ is increasingly obscured by parasitic polarizations at the interface between the liquid and the walls of the sample cell ("electrode polarizations"). Interfacial polarizations largely increase with decreasing frequency[23] and should not be confused with intrinsic properties of the IL. They depend on the conductivity of the sample and on the geometry and materials of the sample cell. For highly conducting samples these effects can extend to several 100 MHz,[10] but in some cases the unperturbed region has extended down to (5 to 20) MHz.[8,24]

Data Evaluation. The dielectric spectra of ILs are dominated by a broad low-frequency mode which, depending on the viscosity of the IL, is centered between 100 MHz and 5 GHz. At the high-frequency edge near 20 GHz there may be wings of modes in the THz regime and modes at intermediate frequencies. Recently, we have described such spectra by the bimodal ansatz[9] $\varepsilon^*(\nu) = \varepsilon_\infty + S_1 \cdot f_1(\nu) + S_2 \cdot f_2(\nu)$, where term 1 describes the low-frequency mode and term 2 forms a global correction for weak high-frequency processes. S characterizes the relaxation amplitude, and $f(\nu)$ describes the spectral distribution.

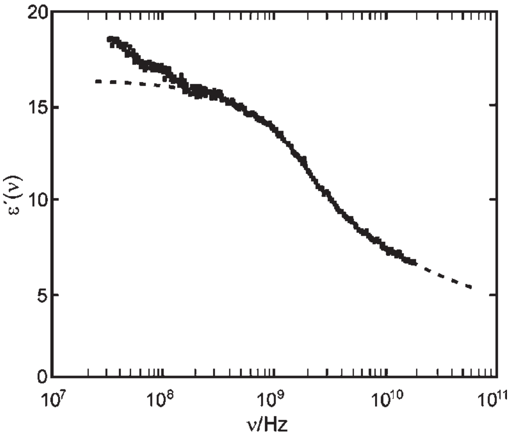

Figure 1. Dielectric dispersion curve of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 25 °C. The dashed line shows the fit by the CC+D ansatz. Below 200 MHz interfacial polarization mimics the onset of a low-frequency mode.

The detailed parametrization provides valuable information on rotational and translational motions of the ions. These aspects will be discussed in forthcoming papers. Here we focus only on the static dielectric constants.

The results for ε are mainly affected by the relaxation model used for parametrizing the low-frequency mode 1 because its functional form controls the asymptotic behavior as $\nu \to 0$. Standard procedures for molecular liquids suggest to describe this mode by an asymmetric Cole–Davidson[1,25] (CD) relaxation time distribution, as adopted in initial studies of the dielectric properties of ILs.[8,9,26,27] As the peculiarities of ion dynamics in ILs are increasingly recognized,[13,14,28] there is evidence that the low-frequency mode is better described by a symmetrical Cole–Cole (CC) relaxation time distribution.[1,25] For a thorough justification we refer to work by Buchner and coworkers.[13,14]

As a consequence, we model here the dominating mode by the CC function

$$f_1(\nu) = 1/\{1 + (i2\pi\nu\tau_1)^{1-\alpha} \tag{2}$$

where τ_1 is a characteristic relaxation time. The exponent $0 \leq \alpha < 1$ controls the width of the relaxation time distribution. For $\alpha = 0$ the CC equation simplifies to the Lorentzian spectral shape associated with a Debye-type exponential relaxation process.[1] In all fits it proved to be sufficient to correct for the wings of high-frequency processes by supplementing the CC mode by a single Debye term (D). While the parametrization of the spectra in terms of the CC rather than CD model does not affect the general physical conclusions, published static dielectric constants have, in part, to be revised because the CC and CD models differ in their asymptotic behavior as $\nu \to 0$.

Experimental Accuracy. Typically, $\varepsilon'(\nu)$ was determined with a precision of ± 0.1 at about (500 to 1000) frequencies. The probe was fixed in a glass cell thermostatted to (298.15 ± 0.02) K. The estimated overall accuracy, including uncertainties in calibration, is ± 0.3. $\varepsilon'(\nu)$ was fitted to the bimodal CC+D ansatz using nonlinear regression.[29] The fitted parameters reproduced the experimental results for $\varepsilon''(\nu)$ within their experimental uncertainty. The residuals of the fits did not show systematic trends, which would indicate a deficiency of the CC ansatz.

The uncertainties of the extrapolated values of ε mainly depend on how close the measurements approach static conditions, e.g. evidenced by the low-frequency plateau of $\varepsilon'(\nu)$. The accessible portion of $\varepsilon'(\nu)$ mainly depended on two factors. First, the useful segment of $\varepsilon'(\nu)$ was limited by uncontrollable interfacial polarizations, which were highly specific in each experiment. Second, the viscosity of the IL formed a crucial factor. The rationale is that a decrease in viscosity shifts the dominant mode to higher frequencies, where it can be better defined and is less subject to errors.[10] As the conductivity usually increases with decreasing frequency, interfacial polarization effects often increase as well. In other words, the two factors mentioned are not independent from one another, leading to a complex interplay of the various phenomena. The error estimates for ε in Table 1 account for the intrinsic uncertainties of $\varepsilon'(\nu)$ and the accessible portion of the dispersion curve of each IL. An idea of the accuracy achieved by this extrapolation is given by the data in Figure 1. For obvious reasons the assigned uncertainties are by an order of magnitude higher than those achieved by standard capacitance methods for molecular solvents.

Note that the accuracy of the quoted results implicitly relies on two assumptions. First, the CC function is assumed to describe the asymptotic behavior of $\varepsilon'(\nu)$ at low frequencies with sufficient accuracy to guarantee reliable zero-frequency extrapolation. Second, it is assumed that there are no dielectric processes below the minimum frequency of the experiment. For many ILs in Table 1 this minimum frequency was of the order of 200 MHz, but taken together, the data in refs 8 and 24 ensure that no further modes are present down to frequencies of the order of 10 MHz. In the kHz regime interfacial polarization becomes huge[23] and prevents any meaningful experiments. The absence of a slow response below the minimum frequency of our experiments is physically plausible for orientational polarization. In case of dielectric spectra of charged systems one may speculate about a low-frequency translational component due to ion migration, but there is currently no conclusive experimental or theoretical evidence for such contributions.[10]

■ RESULTS

Table 1 compiles static dielectric constants of 42 ILs at 25 °C using cation families as an ordering scheme. For 15 ILs marked in the table we have re-evaluated spectra published in an earlier work. All other data refer to measurements within the present study, in parts repeating earlier experiments.

In a few cases we can compare our results with DRS data by Nakamura and Shikata[24] and Hunger et al.[13] This comparison reveals an overall agreement to within a few percent. In general, the extrapolation of $\varepsilon'(\nu)$ based on the CC function yields higher dielectric constants than those obtained by the CD function. An example is 1-butyl-3-methlimidazolium tetrafluoroborate (**13**), where we have to revise the published value[4,5] of $\varepsilon = 11.7$ to $\varepsilon = 13.9$. For the same reason Buchner and coworkers have revised their value for (**13**) from $\varepsilon = 12.2$[27] to $\varepsilon = 14.6$.[13] On the basis of the CC model Nakamura and Shikata reported for (**13**) $\varepsilon = 14.0$.[24] Direct capacitance measurements[30] and voltametry[31] have provided unreliable results.

In a few cases the reparameterization of earlier data by the CC ansatz left ε almost unchanged. For example, data for ethylammonium nitrate[8] (**31**) define the low-frequency plateau of $\varepsilon'(\nu)$ so accurately that the CC and CD functions extrapolate to practically the same value of ε.

■ DISCUSSION

Before direct experimental values of static dielectric constants of ILs became available, estimates of ε have resorted to correlations against other measurable solvent properties. Major examples are correlations deduced from experiments using solvatochromic probe dyes.[32] For some widely used aprotic ILs such as **13** or **14**, these correlations imply polarities similar to those of methanol, acetonitrile, or dimethylsulfoxide. As a consequence many authors assigned to ILs dielectric constant values of the order of $\varepsilon = 30$ to 40.[3] In our initial study[5] we immediately noted that the measured dielectric constants of these aprotic ILs, $\varepsilon = 10$ to 15, are markedly lower than these estimates.

Meanwhile, it is known that low static dielectric constant values are by no means generic for ILs. Like other properties, static dielectric constants can be tuned over a wide range by cation and anion variation. We discuss here the observed trends on a phenomenological level. A detailed molecular-based interpretation is beyond the scope of the present article.

Cation Variation in Aprotic ILs. The effect of cation variation on dielectric constants of aprotic ILs can be assessed from data for ILs with $[\mathrm{NTf_2}]^-$ as a common anion. The key result is that the static dielectric constants of the 1-alkyl-3-methylimidazolium salts **4**, **10**, **15**, and **16** do not differ substantially from those of pyridinium (**23**), pyrrolidinium (**24** to **26**), tetraalkylammonium (**27**, **28**), and trialkylsulfonium (**29**) salts with the same anion. This marginal dependence on the nature of the cation is supported by data for 10 ILs at 70 °C based on the tetra(hexafluoroisopropoxy)aluminate anion reported elsewhere.[33]

Variation of the Alkyl Chain Length of 1-Alkyl-3-methylimidazolium Ions. For the 1-alkyl-3-methylimidazolium salts **4**, **10**, **15**, and **16** with $[\mathrm{NTf_2}]^-$ as a common anion ε increases with increasing length of the alkyl chain. This increase is not evident from the CD-based analysis performed earlier.[9] Results by Nakamura and Shikata[24] for the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium salts, **4** and **15**, perfectly agree with the increase of ε observed by us, and their data for the hexyl- and octyl-based homologues (not measured by us) nicely fit to this trend. Moreover, Nakamura and Shikata[24] reported a similar increase for tetrafluoroborates. Our results for the trifluoromethanesulfonates (**5** and **11**) caution, however, that this dependence on the length of the alkyl chains is not generic.

Methyl Substitution at Carbons C-2, C-4, and C-5 of 1-Alkyl-3-methylimidazolium Salts. In view of the acidity of the hydrogens at carbons C-2, C-4, and C-5 of the imidazolium ring,[2,3] we have considered the effect of methyl substitution at these positions. In case of the pairs (**14**/**17**), (**15**/**20**), and (**13**/**19**) methyl substitution at C-2 has only a weak effect. For the pair (**14**/**18**) a somewhat stronger reduction of ε was found. Marginal effects were also observed for methyl substitution at C-4 and C-5 in the ILs (**21** and **22**). In particular, methyl substitution at C-2 can lead to dramatic changes in some solvent properties, such as the viscosity,[34] and to a pronounced slowing down of molecular motions.[9] The insensitivity of ε to methyl substitution is therefore surprising.

Anion Variation in Aprotic ILs. For aprotic ILs anion variation can resulting more pronounced effects on ε than cation variation, but some results are counterintuitive. The dielectric constants of ILs with symmetrical anions without permanent electric dipole moments, such as $[\mathrm{PF_6}]^-$ or $[\mathrm{BF_4}]^-$, suggest that the modes associated with aprotic cations lead to ε values of the order of $\varepsilon = 12$ to 14. On the basis of these results it is surprising that dielectric constants of ILs with dipolar anions, such as

$[NTf_2]^-$, thiocyanate, or trifluoromethanesulfonate, are of the same order of magnitude. Considering for example 1-butyl-3-methylimidazolium salts, the anions trifluoromethanesulfonate (**11**), thiocyanate (**12**), and $[NTf_2]^-$ (**15**) yield $\varepsilon = 12.9$, 13.7, and 14.0, respectively. Larger effects are observed for oxoanions, such as dimethylphosphate (**3**), butylsulfate (**8**), ethylsulfate (**9**), and (less pronounced) for hydrogen sulfate (**7**). The highest dielectric constant observed so far for an aprotic IL is $\varepsilon = 35.0$ for 1-ethyl-3-methylimidazolium ethylsulfate (**9**). In this case the microwave dielectric spectrum comprises a strong anion mode.[35]

Ammonium-Based Protic ILs. Ethylammonium nitrate (**31**) was the first room temperature molten salt studied by us.[8] Its dielectric constant of $\varepsilon = 26.2$ is substantially higher than those of aprotic ILs with anions of high symmetry. Similar values were later reported by us for a homologous series of alkylammonium formates (**30** to **33**).[21] Table 1 summarizes the revised values based on the CC model. The differences to the published values based on the CD model are quite marginal, except for an error in the published value for butylammonium formate (**33**), which was noted when re-evaluating the data ($\varepsilon = 29.7$ based on the CD model in ref 21 should read $\varepsilon = 22.7$). Obviously, the hydrogen-bonded structure of these ILs enhances the dielectric polarization. A smaller effect is observed for the pyrrolidinium-based protic IL (**34**).

Protic Imidazolium-Based ILs. Protic 1-*H*-3-methylimidazolium chloride (**1**) and the corresponding bromide (**2**) possess lower dielectric constants than protic ammonium salts, presumably due to differences in hydrogen bonding. Yet, the observed ε values are somewhat higher than the dielectric constants of aprotic ILs with anions of high symmetry.

OH-Functionalized ILs. The impression from earlier studies that the static dielectric constants of ILs fall into a narrow range is further vitiated by results for protic ILs with OH-terminated alkyl chains (**35** to **40**). Compared to ethylammonium nitrate (**31**) and ethylammonium formate (**32**) OH-termination of the ethyl group in (2-hydroxyethyl)ammonium nitrate (**36**) and the corresponding formate (**37**) increases the dielectric constants from values near $\varepsilon = 30$ to values near $\varepsilon = 60$, culminating in $\varepsilon = 85.6$ for (2-hydroxyethyl)ammonium lactate (**38**). In molecular liquids such high values are only reached by a few, mainly protic solvents such as water ($\varepsilon = 78.3$). Note that the molar volumes of these ILs are by an order of magnitude larger than that of water, so that the high values of ε are generated by much lower dipole densities than in water. The high dielectric constants may signal strong parallel dipole correlations in the IL structure, which are known to increase ε by co-operative effects, as for molecular liquids described by the well-known Kirkwood theory[36] with Kirkwood correlation factors $g > 1$.

If in the ILs **39** and **40** three 2-hydroxyethyl residues are attached to the ammonium ion instead of a single one, the dielectric constants are somewhat reduced. Again much lower dielectric constants are obtained, if OH-terminated alkyl chains are attached to imidazolium (**41**) and pyridinium (**42**) rings.

CONCLUSIONS

The dielectric constants at 25 °C of the ILs considered in this study fall between $\varepsilon = 10$ and 85. This range is substantially larger than expected on the basis of data available a few years ago.[4] Like many other bulk properties of ILs static dielectric constants can be tuned over wide ranges by cation and anion variation. The following major trends are particularly notable:

Aprotic ILs with anions of high symmetry possess low dielectric constants of the order of $\varepsilon = 10$ to 16. Replacement of highly symmetric anions by some dipolar anions such as $[NTf_2]^-$ has only a marginal effect. Large anion effects, were, however, observed for ILs with oxoanions. The highest dielectric constant for an aprotic IL was observed for 1-ethyl-3-methylimidazolium ethylsulfate ($\varepsilon = 35.0$). Methyl substitution at carbons C-2, C-4, and C-5 of imidazolium rings has only a minor effect.

Protic ILs exhibit higher values than aprotic ILs, typically resulting in $\varepsilon = 20$ to 30 for monoalkylammonium salts. The highest dielectric constants were obtained for some OH-functionalized alkylammonium salts, culminating in $\varepsilon = 85.6$ for (2-hydroxylethyl)ammonium lactate.

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