Measured relative complex permittivities for multiple series of ionic liquids

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ABSTRACT

Presented in this paper are experimentally measured relative complex permittivities as a function of frequency for a representative range of ionic liquids, comprising 64 imidazolium, choline, phosphonium, ammonium, pyrrolidinium, pyridinium and piperidinium cations with a variety of anions. The measurement was conducted using a coaxial probe technique at room temperature from almost DC (0 Hz) to 18 GHz with a high level of accuracy. The real parts of the complex permittivities have been summarized in table format with both the real and imaginary parts presented as individual spectra for each ionic liquid. It is found that an increase in the molecular weight results in a decrease in overall permittivity and this is true over multiple series of ionic liquids. Additives such as water are shown to have a profound effect on the complex permittivity. The measured data is useful for a wide range of applications, such as electronic devices, chemical synthesis and materials.

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1. Introduction

The behaviour of molecules under the influence of electromagnetic waves at frequencies > 1 THz has been extensively studied in the field of physical chemistry and closely related subjects using techniques such as infra-red and UV–visible spectroscopy [1]. However, the influence of radio and microwave frequencies on the behaviour of molecules, such as relative complex permittivity, is comparatively less researched or considered, especially in the field of chemistry. The relative complex permittivity of a material provides useful information on the dielectric relaxation and absorption processes that are prevalent in a wide frequency range. Information relating to polarity, conductivity, dielectric loss, ionic/dipolar relaxations and atomic/electronic resonances can be deduced from the complex permittivity spectrum of a given material [2]. Relative complex permittivity (ε_r) can be defined as in Eq. (1), where ε is the absolute permittivity and ε_0 is the vacuum permittivity (often referred to as the permittivity of free space). The value of ε_0 is fixed at 8.85×10^{-12} F/m. The real and imaginary parts of the relative complex permittivity are experimentally measured and denoted by ε' and ε'', respectively, and ω describes the dependence upon frequency and is called angular frequency which is $\omega = 2\pi f$.

$$\varepsilon_r(\omega) = \frac{\varepsilon(\omega)}{\varepsilon_0} = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{1}$$

Complex permittivity is a very important material property for electromagnetics and related subjects. Data derived from relative complex permittivity measurements have been utilized in applications, such as liquid antennas including our recent work [3–5], radio-frequency and microwave devices [6], lithium batteries [7], carbon nanotube (CNT) microwave absorbers [8] and even field-deployable sensors for the detection of improvised explosives [9]. The availability of accurate permittivity data, both static (i.e. 0 Hz, or direct current (DC)) and as a function of frequency, for ionic liquids (ILs) and other solvents, liquids and materials, will play a vital role in the development and discovery of new technologies and spectroscopic techniques.

Dielectric loss describes the inherent dissipation of electromagnetic energy by a material and can be defined by the loss tangent ($\tan\delta_e$) as in Eq. (2). It is typically frequency-dependent and parametrized using the real and imaginary parts of the relative complex permittivity as described in Eq. (1). For time-varying electromagnetic fields, the electromagnetic energy is typically viewed as waves propagating either through free space, in a transmission line, or through a waveguide. Dielectrics are often used in all of these environments to mechanically support electrical conductors and keep them at a fixed separation. In these scenarios, the electromagnetic energy is often dissipated in the form of heat.

$$\tan\delta_e = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}. \tag{2}$$

The relative permittivity of a material at 0 Hz is referred to as the static relative permittivity (often called the static dielectric constant) and is normally derived by extrapolation of values measured at higher

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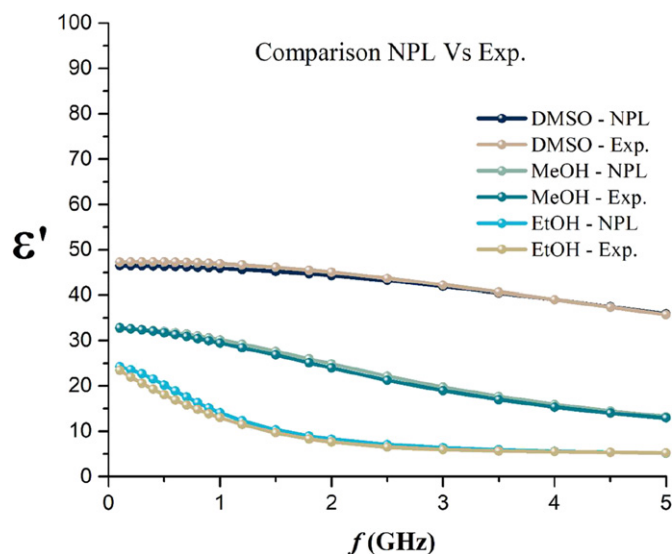 E-mail address: jxiao@liverpool.ac.uk (J. Xiao).
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frequencies. It can also be measured through techniques such as capacitance measurements of a capacitor at DC (0 Hz). There are many literature sources that report static dielectric constants of organic molecules [10], solvents [11], binary mixtures [12] but far fewer for ILs [13].
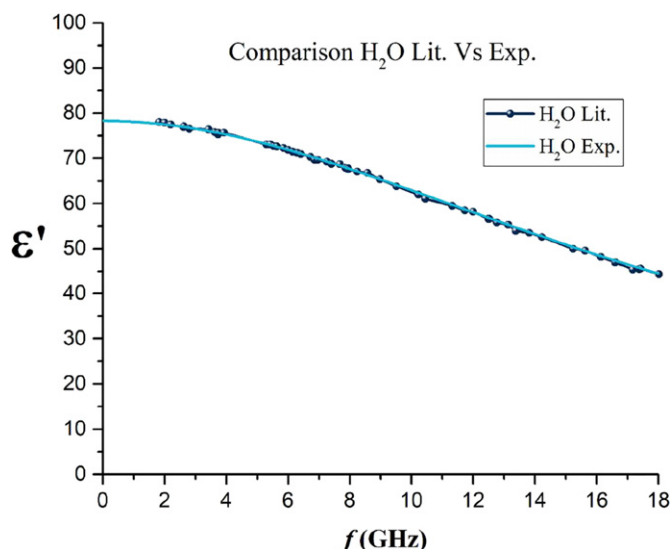
ILs are generally described as salts completely comprised of ions with melting points lower than 100 °C, although the term room temperature ionic liquid (RTIL) has been more commonly used recently and invokes a much lower melting temperature [14]. First reported by Walden over 100 years ago (ethylammonium nitrate, mp 12 °C [15]), they have received a huge increase in interest over the last two decades, with over 5000 publications in 2016 alone. They boast highly desirable properties, such as a wide liquid range, extremely low volatility, good conductivity, excellent electrochemical windows, tunable polarity, thermal stability and low flammability. They have been described as "designer solvents" and due to the anionic/cationic combinatorial nature of their preparation, they can be customized to almost any desired requirements [16,17]. Thousands of articles utilizing ILs have been reported in the fields of energy, materials, nano-area, electrochemistry and catalysis with novel and more niche applications arising regularly [18]. Recent articles with novel applications of ILs include battery technologies [19], metal-organic frameworks (MOFs) [20], separation of rare-earth minerals [21] and an ever increasing amount of research in the field of catalysis [22].

The static dielectric constants of ionic liquids have been reported [13,23–33], with updated values found in more recent publications [23,24,29,30]. There appear to be some discrepancies within the literature over the accuracy of values derived using various measurement techniques, such as microwave dielectric spectroscopy and polarity-sensitive fluorescent molecular probes. This variation has reportedly been linked to their inherent conductivity which can essentially short-circuit the system when directly measuring ε using fluorescent probes [34,35]. To the best of our knowledge, there are no studies of complex permittivity (i.e. frequency dependent dielectric constants) reported for pure ILs so far, except for the original IL N_{HHH2} NO_3 [36]. This study aims to provide data on the dielectric behaviour of ILs as a function of frequency.

Static dielectric constants are a useful indicator of polarity, often presented along with dipole moment or polarity index values. However, complex permittivity (over a broad frequency range) can provide additional information vital to many chemical and electrical engineers. Recently we have demonstrated, for the first time, that ILs can be used to fabricate dielectric resonator antennas (DRAs) with their performance inherently linked to their frequency-dependent dielectric constants
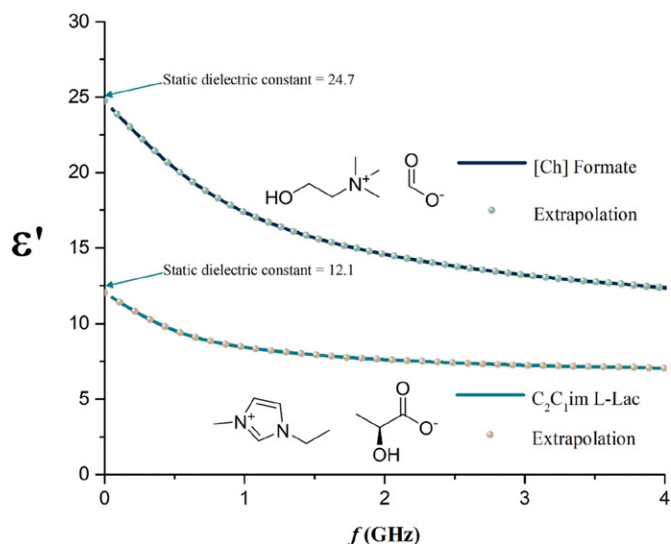

Fig. 2. A comparison of the real part of relative complex permittivity (ε') of H_2O at 25 °C up to 18 GHz between the literature [40] and this work (Exp.).

and the loss factor derived from the real and imaginary parts of the permittivity spectrum (Eq. (2)) [4,5].

Herein we report the experimentally derived complex permittivity data of 64 imidazolium, choline, phosphonium, ammonium, pyrrolidinium, pyridinium and piperidinium ILs in the range of 1 to 18 GHz and extrapolated static values at 0 Hz (measured down to 30 KHz). The information disclosed will be of value when selecting a material for engineering applications which require precise electromagnetic properties.

2. Experimental and methods

There are a number of methods for permittivity measurements with their pros and cons. One of the most suitable methods for liquid material measurement is the open-end coaxial probe approach which has been used for our study [37,38]. It gives a high degree of accuracy over a wide frequency range. We used an Agilent N9917A FieldFox Microwave Vector Network Analyser (VNA) and a Keysight 85070E Dielectric Probe Kit [39]. The measurement frequency range of the instrument was set from 30 kHz to 18 GHz with 1001 data points. The radio-frequency

Fig. 1. A comparison of the real parts of relative complex permittivities (ε') for dielectric reference liquids DMSO, MeOH and EtOH between the data from the NPL [37] and this work (Exp.) up to 5 GHz.

Fig. 3. A graphical example of the extrapolation procedure used to determine the static dielectric constants.

Table 1
Comparison of experimental static dielectric constants derived in this study with values found in the literature.

| Liquid	Static ε' Exp.	Static ε' Lit.	[Refs]
H$_2$O	78.3	77.9–79.5	[42,43]
DMSO	46.2	45.9–48.8	[44,45]
Acetone	20.1	19.1–20.8	[46,47]
DMF	38.1	36.7–40.2	[45,48]
Acetonitrile	35.8	34.3–37.0	[49,50]
Propylene Carbonate	64.9	63.0–65.5	[10,51]

output power level of the VNA was set to 0 dBm. A 3-point calibration method was employed which was comprised of open-circuit (in air), short-circuit (calibration block) and 25 °C distilled water measurements and as per the manufacturer's guidelines. Each unknown sample was measured using multiple probes and after repeated calibrations to confirm identical permittivity spectra were obtained. All measurements were conducted at 25 °C (unless otherwise stated) under an inert nitrogen atmosphere. The liquid samples were dried in a vacuum oven for > 24 h prior to use and held using 10 mL standard lab glass vials with PTFE lined caps. The probe was immersed into the IL samples with a depth of 20–30 mm from the liquids surface. The relative

complex permittivities of the compounds, including the real and imaginary parts, were measured accordingly.

To ensure reliability of results before measuring unknown liquid samples, compounds with well-defined relative complex permittivity spectra found in the literature were first measured. These reference liquids include dimethyl sulfoxide (DMSO), methanol (MeOH) and ethanol (EtOH), the dielectric constants of which have been described to a high degree of accuracy by the National Physical Laboratory (NPL, U.K.) up to a frequency of 5 GHz [37]. As shown in Fig. 1, our experimentally measured results are in excellent agreement with the literature (Fig. 1).

A further comparison with the literature data, recreated from the tables in reference [40], can be seen in Fig. 2, using H$_2$O measured at 25 °C up to 18 GHz, which is also the high frequency limit of our presented data. Again our data shows excellent agreement with the literature across the broad measured frequency range.

The dielectric constants presented in Tables 2–6 (vide infra) within the frequency range of 1–18 GHz are taken directly from the experimentally measured data. The reported dielectric constants in the tables at 0 Hz (static dielectric constants) were extrapolated from the experimental data (measured down to the low frequency of 30 KHz, which is the approximate accuracy range of the Keysight 85070E Dielectric Probe Kit [39]). The polynomial curve fitting (PCF) method of MATLAB®2017 was
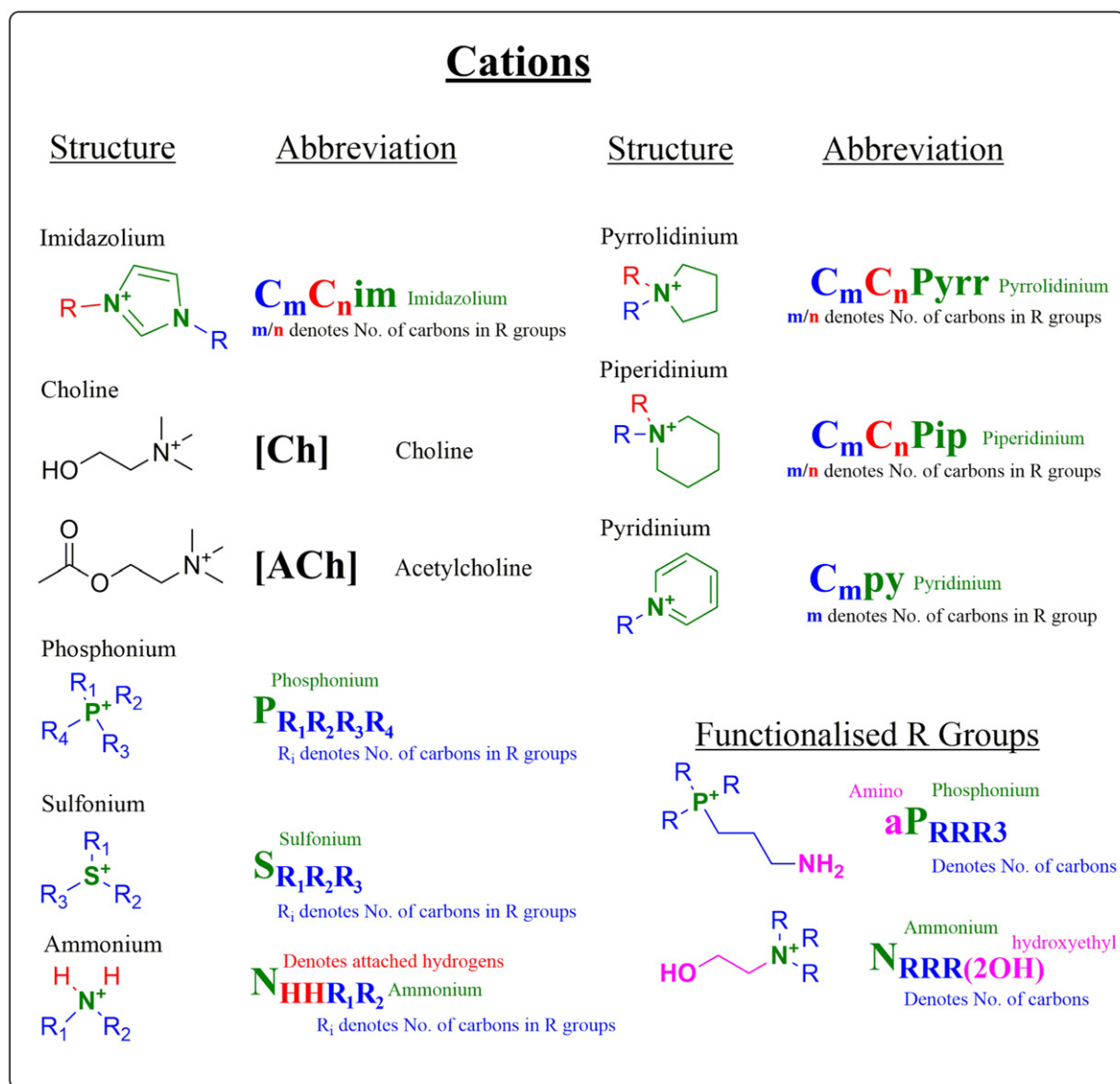
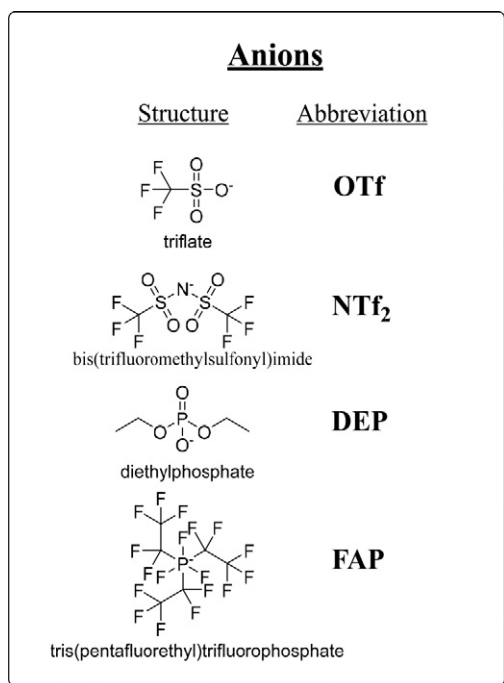**Fig. 4.** Nomenclature for abbreviated IL cations.

Fig. 5. Structures and abbreviations for complex anions.

Fig. 6. Effect of increasing chain length on the real part of the permittivity (ε') for (a) $C_nC_1$im BF_4 & (b) $C_nC_1$im NTf_2 IL series.

then employed to extrapolate the values. An example of this low frequency extrapolation can be seen in Fig. 3, where the solid line represents the experimental data and the markers indicate the extrapolated values.

In order to validate the accuracy of our results, the same measurement and extrapolation procedures were employed for selected common liquid materials with static dielectric constants well defined in the literature by a myriad of sources. The static dielectric constants derived using our method were found to be in excellent agreement with the literature

sources; a comparison between the experimental and literature values is shown in Table 1. The reference values presented in Table 1 are the highest and lowest published static dielectric constants available; however, it should be noted that the vast majority of the literature values generally lie somewhere between. The liquids chosen include those with negligible contributions from the imaginary part (ε'') of the complex permittivity (i.e. acetonitrile) and those with considerable imaginary

Table 2
Dielectric constants of imidazolium ionic liquids as a function of frequency.

	Ionic liquid	0[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
																				f (GHz)
ε	C_2C_1im BF_4	12.9	11.7	11.0	10.5	10.2	9.9	9.7	9.5	9.4	9.2	9.1	9.0	8.9	8.7	8.5	8.3	8.1	7.9	7.7
	C_2C_1im CH_3CO_2	16.3	13.0	11.5	10.7	10.1	9.7	9.4	9.1	8.9	8.7	8.5	8.4	8.3	8.2	8.1	8.0	7.9	7.9	7.9
	C_2C_1im $EtOSO_3$	24.4	13.3	11.1	10.1	9.4	9.0	8.7	8.4	8.2	7.9	7.8	7.7	7.5	7.4	7.4	7.3	7.2	7.1	7.1
	C_2C_1im $N(CN)_2$	12.5	11.8	11.1	10.5	9.9	9.5	9.1	8.9	8.6	8.4	8.3	8.1	8.0	7.9	7.8	7.7	7.7	7.6	7.5
	C_2C_1im OTf	19.3	14.1	12.7	11.6	10.9	10.3	9.9	9.6	9.3	9.1	8.8	8.6	8.4	8.2	7.9	7.6	7.4	7.1	6.9
	C_2C_1im NTf_2	13.8	11.5	9.9	8.9	8.3	7.8	7.4	7.1	6.9	6.7	6.5	6.4	6.3	6.2	6.1	6.0	6.0	5.9	5.9
	C_2C_1im SCN	15.1	13.8	12.8	11.9	11.2	10.7	10.2	9.9	9.6	9.3	9.2	9.0	8.8	8.7	8.6	8.5	8.4	8.3	8.3
	C_2C_1im DEP	8.1	6.8	6.3	6.0	5.9	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.7	5.7	5.6	5.6	5.5
	C_2C_1im L-Lac	12.1	8.5	7.6	7.2	7.0	6.9	6.9	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.7	6.6	6.6	6.5	6.5
	C_2C_1im $FeCl_4$	13.1	9.6	8.5	7.9	7.5	7.3	7.2	7.0	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.3	6.2	6.1	6.0
	C_2OHC_1im OTf	20.7	11.6	9.8	8.8	8.3	8.1	7.9	7.7	7.6	7.5	7.4	7.3	7.2	7.2	7.1	6.9	6.7	6.6	6.6
	C_2OHC_1im PF_6	9.9	7.9	7.3	7.0	6.8	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.6	6.5	6.5	6.5
	C_3C_1im I	5.5	5.2	5.2	5.2	5.2	5.2	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1
	C_3C_1im NTf_2	9.4	8.1	7.2	6.7	6.3	6.1	6.0	5.9	5.8	5.7	5.7	5.6	5.5	5.5	5.4	5.3	5.2	5.1	5.0
	C_3OC_1im PF_6	8.6	7.6	7.1	6.8	6.7	6.6	6.5	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.3	6.2	6.2	6.1	6.1
	C_4C_1im BF_4	9.7	8.8	8.1	7.7	7.5	7.3	7.2	7.2	7.1	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.5	6.4
	C_4C_1im SCN	9.7	8.4	7.7	7.3	7.0	6.9	6.8	6.7	6.7	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.2
	C_4C_1im L-Lac	6.6	5.6	5.4	5.3	5.3	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
	C_4C_1im $MeOSO_3$	11.9	8.7	7.8	7.3	7.1	7.0	6.9	6.8	6.8	6.8	6.7	6.7	6.7	6.7	6.6	6.5	6.4	6.4	6.4
	C_4C_1im $N(CN)_2$	10.3	9.4	8.7	8.2	7.9	7.6	7.5	7.4	7.3	7.2	7.1	7.1	7.0	6.9	6.8	6.6	6.5	6.4	6.3
	C_4C_1im NTf_2	9.2	8.2	7.4	6.8	6.4	6.2	6.0	5.9	5.8	5.7	5.6	5.5	5.5	5.5	5.4	5.4	5.4	5.4	5.4
	$C_4C_1C_1$im NTf_2	8.8	7.5	6.7	6.2	5.9	5.7	5.6	5.5	5.4	5.3	5.2	5.2	5.2	5.1	5.1	5.1	5.1	5.1	5.1
	C_6C_1im BF_4	8.4	7.5	6.9	6.5	6.3	6.1	5.9	5.8	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.3
	C_6C_1im NTf_2	8.5	7.6	6.8	6.2	5.9	5.6	5.4	5.3	5.1	5.0	4.9	4.9	4.8	4.7	4.7	4.6	4.6	4.6	4.6
	C_6C_1im PF_6	7.1	6.4	5.9	5.6	5.5	5.3	5.2	5.1	5.0	4.9	4.9	4.9	4.8	4.8	4.7	4.7	4.7	4.7	4.7
	C_6C_1im I	4.3	4.3	4.3	4.3	4.3	4.3	4.4	4.4	4.5	4.5	4.6	4.6	4.7	4.7	4.7	4.7	4.7	4.8	4.8
	C_8C_1im NTf_2	6.9	6.0	5.4	5.1	4.8	4.7	4.6	4.5	4.4	4.3	4.3	4.2	4.2	4.2	4.2	4.2	4.1	4.1	4.1
	C_8C_1im Cl	3.2	3.3	3.5	3.6	3.6	3.7	3.7	3.8	3.8	3.9	4.0	4.0	4.1	4.1	4.1	4.1	4.2	4.2	4.3

All measurements performed at 298 K, under an inert $N_{2(g)}$ atmosphere. See supplementary data for imaginary parts of the dielectric spectra and full plotted graphs.

[a] Static dielectric constants derived by polynomial extrapolation; see experimental section, Fig. 3 and Table 1 for details.
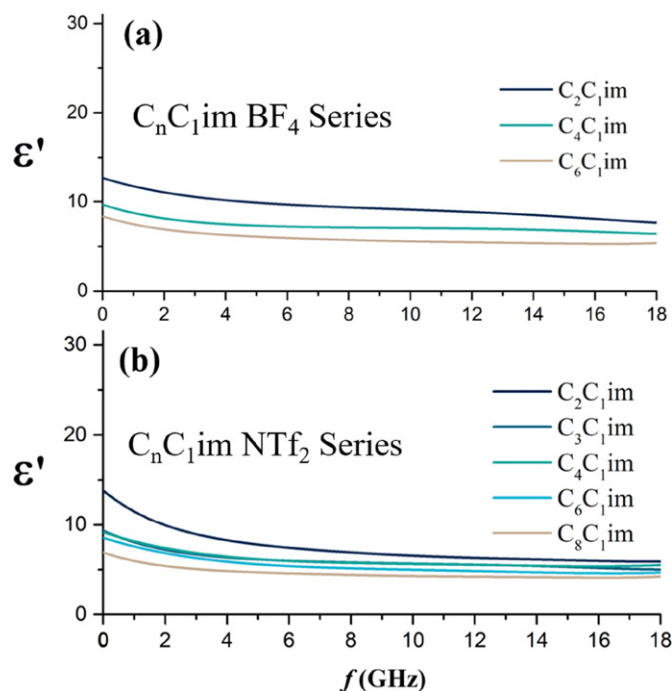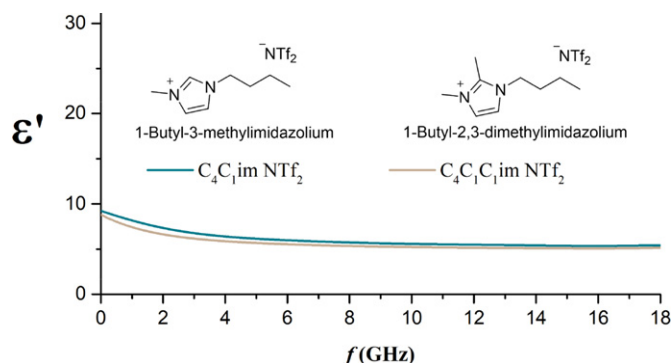
Fig. 7. Effect of a methyl group on the complex permittivity of butyl-imidazolium NTf$_2$ ILs.

contributions (i.e. propylene carbonate). It should also be noted that our experimental values of these liquid materials are also in excellent agreement with those available in the literature at higher frequencies, which further confirms the validity of the measured results within this paper [40,41].

For full details of the 64 commercially available and synthesized ILs used in this study, please see the Supplementary Data file (Appendix A), which includes the full structures, chemical names, abbreviated names, synthetic procedures and characterisation data. Appendix A also includes individual spectra for all ILs measured containing both real (ε') and imaginary (ε'') parts of the relative complex permittivity (ε_r).

3. Results and discussion

Due to the cationic/anionic nature of IL structures and the huge number of possible combinations, including their associated long chemical names, an abbreviation system is often used. Fig. 4 gives a structural breakdown of the abbreviations used for IL cations in this study. 1-Ethyl-3-methylimidazolium, for example, has previously been abbreviated as EMIM; however, using the ethyl/methyl description would not suffice for some alkyl chains, such as propyl/pentyl. More recently a numbered R-group carbon system has been implemented and we have tried to stick to this naming system herein [52], e.g. EMIM now described as C$_2$C$_1$im.

For anion abbreviations, structural or molecular formulae work for most common anions, such as tetrafluoroborate (BF$_4$) or formate (HCO$_2$). Fig. 5 gives the structures associated with more complex anions and their abbreviations. When the source of the anion is an amino acid (AA), the standard 3-letter abbreviations have been used, i.e. L-Alaninate written as L-Ala.

A full list of IL structures, chemical names and abbreviations can be found in the supplementary data file (Appendix A).

Air and moisture stable imidazolium ILs are some of the most studied and commercially available classes of IL. From the results presented in Table 2, we can see the effect that increasing the imidazolium alkyl chain length has on the dielectric constant. In two of the most common IL series, C$_n$C$_1$im with BF$_4$ anions and also with NTf$_2$ anions, there is a significant drop in the overall permittivity when increasing alkyl chain length and therefore molecular weight, which can be further seen in Fig. 6. Literature sources have shown that increasing alkyl chain length on imidazolium ILs results in an increase in viscosity, and this reduction in ionic mobility also correlates to a decrease in the overall polarity as well as electrical conductivity [53].

The 2-position of imidazolium ILs are known to be reasonably acidic [56,57]. This inherent acidity and the ability to generate NHC-type carbenes have been utilized in transition metal catalysis [58,59], although any non-innocent side reactions of ILs would generally be considered unwanted in the vast majority of IL applications. Fig. 7 shows the negligible effect of 2-position methylation on the permittivity of butyl-imidazolium ILs with NTf$_2$ anions. An insignificant change in the overall permittivity spectrum and polarity can be deduced, implying that if required, one may substitute for a similar yet more chemically stable IL without sacrificing a polar environment.

Table 3 shows the relative complex permittivity measurements of choline ([Ch]) amino-acid (AA) or related carboxylic acid ILs. The general trend revealed implies again, that increasing molecular weight results in a decrease in frequency-dependent dielectric constants. This trend is observable in Fig. 8. Individual viscosity and conductivity values for specific ILs vary considerably across multiple literature sources. For example, Ch L-Pro has published viscosity values ranging between 0.5 [60] and 10.64 [61] Pa·S and conductivity values from 0.3 [61] to 7.5 [62] μS cm^{-1}. Thus, although there appears to be a correlation between increased molecular weight and decreased dielectric constants (also see Fig. 6), any correlation of dielectric constants with the literature values of viscosity or conductivity should be cautious [60–66].

The complex permittivities of these completely organic [Ch] AA ILs have extremely small contributions from their imaginary parts (ε''), which give these liquids somewhat unique properties among ILs (see supplementary data for full spectra displaying ε' & ε''). Compared to the commonly used imidazolium series, they exhibit extremely low loss (see Eq. (2)) and very low electrical conductivity (σ_{ac}), which can be calculated as in Eq. (3), where $\varepsilon'\varepsilon_0$ represents the real part of the absolute permittivity.

$$\sigma_{ac} = \omega\varepsilon'(\omega)\varepsilon_0 \tan\delta_e \tag{3}$$

The phosphonium ILs found in Table 4 all exhibit very little dielectric relaxation with stable permittivities over the full range measured up to

Table 3
Dielectric constants of choline ionic liquids as a function of frequency.

									f (GHz)										
	Ionic liquid	0[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	[Ch] HCO$_2$[b]	24.7	17.4	14.6	13.2	12.4	11.8	11.4	11.0	10.8	10.7	10.5	10.4	10.3	10.2	10.1	10.0	9.9	9.9	9.9
	[Ch] L-Ala	31.4	10.6	9.4	8.7	8.3	8.0	7.8	7.6	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.9
	[Ch] L-Cys	9.5	7.3	6.8	6.5	6.3	6.2	6.1	6.0	6.0	5.9	5.9	5.9	5.9	5.9	5.9	5.9	5.9	5.9	5.9
	[Ch] L-His	9.1	7.1	6.6	6.3	6.1	5.9	5.8	5.7	5.7	5.6	5.6	5.6	5.5	5.5	5.5	5.5	5.5	5.5	5.5
	[Ch] L-Lac	20.4	9.6	8.6	8.0	7.7	7.4	7.2	7.1	7.0	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.5
ε	[Ch] L-Lys	9.8	8.3	7.4	7.0	6.7	6.5	6.4	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.9	5.9	5.8	5.8	5.8
	[Ch] L-Phe	14.8	7.6	6.9	6.5	6.3	6.1	6.0	5.9	5.8	5.8	5.7	5.7	5.7	5.7	5.6	5.6	5.6	5.6	5.5
	[Ch] L-Pro	12.6	8.2	7.4	7.0	6.7	6.5	6.4	6.3	6.2	6.1	6.1	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	[Ch] L-Tryp	7.7	6.4	6.0	5.8	5.6	5.5	5.4	5.3	5.3	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.1
	[Ch]Cl/Urea[c]	9.8	8.9	8.3	7.8	7.5	7.3	7.2	7.1	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.6	6.6	6.6
	[ACh] NTf$_2$	17.5	8.5	7.4	6.9	6.5	6.2	6.1	5.9	5.9	5.8	5.7	5.6	5.6	5.6	5.6	5.6	5.5	5.5	5.6

All measurements performed at 298 K, under an inert N$_{2(g)}$ atmosphere. See supplementary data for imaginary parts of the dielectric spectra and full plotted graphs.
[a] Static dielectric constants derived by polynomial extrapolation; see experimental section, Fig. 3 and Table 1 for details.
[b] Measured at 311 K (liquid state of compound).
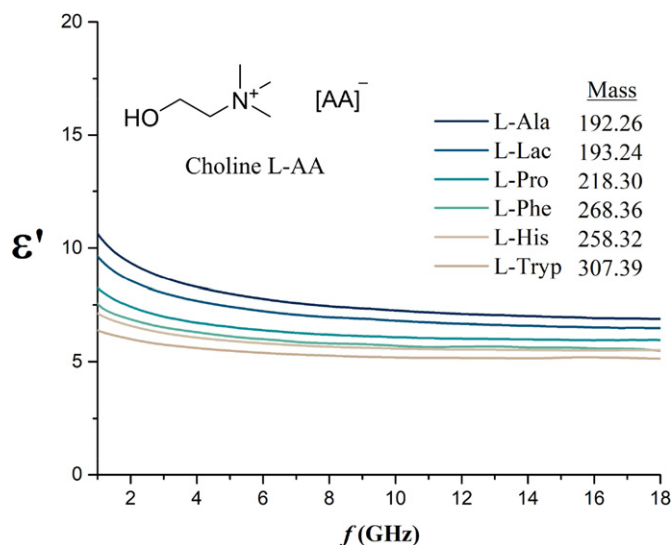[c] Choline chloride:Urea in a 1:2 ratio, deep eutectic solvent (DES) [54].

Fig. 8. Complex permittivity spectra of Choline AA IL series.

18 GHz. The dielectric constants are small and lie between ≈ 3–8, and the phosphonium series also possess extremely small imaginary parts and therefore dielectric loss. This is in contrast to the sulfonium IL included in Table 4, which shows some dielectric relaxation from low to high frequencies and also has more contributions from the imaginary part. Therefore, this sulfonium IL can be considered a more dielectrically lossy and electrically conductive material.

Table 5 presents the results for ammonium based ILs. It appears that N_{HHH2} NO_3, the original IL discovered in 1914, has one of the largest overall complex permittivities across the full frequency range. It has a comparatively large static dielectric constant, which is smaller still

than its imaginary part (see supplementary data), and therefore is extremely lossy, especially at frequencies < 9 GHz. It has, however, been used as a conductive solvent in electrochemistry; so the large imaginary contribution is expected, Eq. (3) [67]. $N_{HHH(2OH)}$ HCO_2 exhibits similar properties to N_{HHH2} NO_3 and shows a sharp dielectric relaxation as the frequency increases and with reports in the literature stating a conductivity of ≈ 0.34 S/m, the large imaginary contribution is again rationalized and expected [68]. There is a contrast between this formate IL and the very closely related $N_{HHH(2OH)}$ CH_3CO_2 which differs only from a change in anion from formate to acetate. The broadband permittivity of the latter is significantly lower, and the material is much less electrically conductive and lossy. This could be explained by the vastly different viscosities, with the formate analogue having a much greater fluidity compared to the viscous acetate IL. The extra mobility of charge carriers obviously contributes to the conductivity, and the extra methyl group located within the anion could be said to contribute to the reduction in the overall polarity. The rest of the ammonium series progresses as expected, with additional alkyl groups of increasing length, and also with hydroxyl functionality, significantly reducing the dielectric relaxation and imaginary contributions. This is highly likely due to the increase in mass and the hydrogen bonding contributions both intra- and inter-molecularly from the –OH and – NH groups where relevant.

Table 6 presents the results for pyrrolidinium, pyridinium and piperidinium ILs which exhibit similar dielectric properties. They lie within the range of $\varepsilon' ≈ 5$–10 with the highest found for C_4C_1Pyrr OTf. The other results are as expected with the largest imaginary contributions found for ILs with anions linked to greater electrical conductivities, i.e. OTf, $N(CN)_2$ and NTf_2.

Values for extrapolated static dielectric constants (0 Hz frequency) found in the literature often vary. Table 7 shows a comparison between values derived in this study with those for the same ILs found within multiple literature sources.

Table 4
Dielectric constants of phosphonium & sulfonium ionic liquids as a function of frequency.

	Ionic liquid	0[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
												f (GHz)									
ε	aP_{4443} HCO_2	6.4	5.8	5.4	5.2	5.1	5.0	4.9	4.9	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8
	aP_{4443} CH_3CO_2	5.5	5.3	5.1	5.0	4.9	4.8	4.7	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
	aP_{4443} L-Lac	5.1	4.9	4.7	4.6	4.5	4.4	4.4	4.4	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
	aP_{4443} L-Val	8.3	6.8	6.2	5.8	5.6	5.4	5.3	5.2	5.1	5.1	5.0	5.0	4.9	4.9	4.9	4.9	4.8	4.8	4.8
	P_{4441} $MeOSO_3$	5.5	5.2	5.1	5.0	5.0	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
	$P_{666(14)}$ Cl	3.6	3.5	3.5	3.4	3.3	3.3	3.2	3.2	3.2	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.0
	$P_{666(14)}$ NTf_2	4.9	4.3	4.0	3.8	3.7	3.6	3.5	3.5	3.4	3.4	3.4	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
	S_{222} NTf_2	14.0	11.7	10.2	9.2	8.5	8.1	7.7	7.4	7.2	7.0	6.9	6.7	6.6	6.5	6.4	6.4	6.3	6.2	6.2

All measurements performed at 298 K, under an inert $N_{2(g)}$ atmosphere. See supplementary data for imaginary parts of the dielectric spectra and full plotted graphs.
 [a] Static dielectric constants derived by polynomial extrapolation; see experimental section, Fig. 3 and Table 1 for details.

Table 5
Dielectric constants of ammonium ionic liquids as a function of frequency.

	Ionic Liquid	0[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
												f (GHz)									
ε	N_{HHH2} NO_3	25.4	20.0	16.6	14.5	13.3	12.5	11.9	11.5	11.1	10.8	10.6	10.4	10.2	10.1	9.9	9.8	9.7	9.6	9.5
	$N_{HHH(2OH)}$ HCO_2	80.5	28.9	19.2	15.4	13.3	12.3	11.5	10.8	10.4	10.1	9.9	9.6	9.3	9.2	9.2	9.0	8.9	8.9	8.9
	$N_{HHH(2OH)}$ CH_3CO_2	8.7	6.8	6.3	6.0	5.8	5.7	5.7	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
	$N_{HHH(2OH)}$ L-Lac	8.3	7.0	6.3	5.9	5.6	5.4	5.2	5.1	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	$N_{(2OH)(2OH)(2OH)1}$ $MeOSO_3$	24.9	11.6	9.9	9.0	8.6	8.2	8.0	7.7	7.6	7.5	7.4	7.2	7.2	7.2	7.2	7.1	7.1	7.1	6.8
	$N_{(2OH)(2OH)(2OH)1}$ L-Pro	6.4	5.9	5.6	5.4	5.3	5.2	5.2	5.1	5.0	5.0	5.0	5.0	5.0	5.0	4.9	4.9	4.9	4.9	4.8
	N_{8881} NTf_2	5.4	4.4	4.1	3.9	3.8	3.7	3.6	3.6	3.5	3.5	3.5	3.5	3.5	3.4	3.4	3.4	3.4	3.4	3.4
	$N_{122(2O1)}$ BF_4	8.8	7.5	7.0	6.8	6.7	6.6	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.4	6.3	6.3	6.3
	DIMCARB[b]	12.6	9.7	8.6	8.0	7.6	7.3	7.2	7.0	6.9	6.8	6.7	6.7	6.7	6.7	6.6	6.6	6.6	6.6	6.6

All measurements performed at 298 K, under an inert $N_{2(g)}$ atmosphere. See supplementary data for imaginary parts of the dielectric spectra and full plotted graphs.
 [a] Static dielectric constants derived by polynomial extrapolation; see experimental section, Fig. 3 and Table 1 for details.
 [b] DIMCARB:Dimethylammonium dimethylcarbamate in a 1:1 ratio, distillable ionic liquid [55].

Table 6
Dielectric constants of pyrrolidinium, pyridinium and piperidinium ionic liquids as a function of frequency.

	Ionic Liquid	f (GHz)																		
		0^a	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ε	C_4C_1Pyrr OTf	10.5	9.1	8.2	7.7	7.4	7.2	7.0	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.4	6.3	6.1	6.0	6.0
	C_4C_1Pyrr N(CN)$_2$	8.1	7.8	7.3	7.0	6.8	6.7	6.6	6.5	6.4	6.4	6.4	6.4	6.4	6.3	6.2	6.1	6.0	6.0	6.0
	C_4C_1Pyrr FAP	5.3	5.0	4.7	4.5	4.4	4.4	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.2	4.2	4.2
	C_4–3-MePyrr NTf$_2$	7.9	7.1	6.5	6.1	5.9	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.2	5.1	5.0	5.0	5.0
	C_6py BF$_4$	5.7	5.5	5.4	5.3	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
	C_6py NTf$_2$	6.0	5.6	5.2	5.0	4.8	4.7	4.7	4.7	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.5	4.5	4.5	4.5
	C_4-3-Mepy MeOSO$_3$	9.5	7.6	7.1	6.8	6.7	6.6	6.5	6.5	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.3	6.2	6.2	6.2
	C_3C_1Pip NTf$_2$	6.8	5.9	5.5	5.2	5.0	4.9	4.9	4.8	4.8	4.8	4.8	4.8	4.8	4.7	4.7	4.6	4.6	4.6	4.6

All measurements performed at 298 K, under an inert $N_{2(g)}$ atmosphere. See supplementary data for imaginary parts of the dielectric spectra and full plotted graphs.

[a] Static dielectric constants derived by polynomial extrapolation; see experimental section, Fig. 3 and Table 1 for details.

The comparison of static dielectric constants shows a varied agreement with the literature. Some ILs are in good agreement. Our experimental value for S_{222} NTf$_2$ of 14.0 lies neatly between the two reported literature values of 13.2 and 15.8, which were from the same laboratory. Other ILs, such as C_2C_1im BF$_4$, C_2C_1im N(CN)$_2$ and N_{HHH2} NO$_3$, are in good to excellent agreement with multiple literature sources, and values for N_{HHH2} NO$_3$ are also in excellent agreement at higher frequencies [36]. It can be noted that our values for higher order alkyl imidazoliums (such as C_4C_1im BF$_4$ and NTf$_2$) are often slightly lower than those of the literature.

It has been previously reported that the addition of water to ILs has little effect on the permittivity and that at IL weight fractions above 0.75, the static dielectric constant is rather insensitive to the water content [24,25]. This assertion was deduced using $N_{HHH(2OH)}$ HCO$_2$ as an example which already possesses a static permittivity close to that of H_2O; thus the effect of water might be less visible. However, this may not be the case with other ILs with typically significantly lower static values, especially the protic ionic liquids (PILs) or those capable of hydrogen bonding. Indeed, significant changes in the permittivity spectra are

observed. As shown in Fig. 9, the effect of increasing concentrations of H_2O on the complex permittivity spectra of the PILs $N_{HHH(2OH)}$ formate and acetate is clearly visible. Although the effect on the static permittivity with respect to the formate analogue is negligible (80.5 for neat IL and 82.6 for a 50:50 IL:H_2O mixture), the overall complex permittivity spectra are significantly altered when the concentration of highly polar H_2O is increased. The effect is more dramatic on both the static and complex permittivity for the acetate analogue, which possesses a significantly lower static dielectric constant in its anhydrous form (8.7 for neat IL and 75.2 for a 50:50 IL:H_2O mixture).

Table 7
Comparison of IL static dielectric constants derived in this study with values found in the literature.

IL	Static ε' Exp.	Static ε' Lit. [Ref]
C_2C_1im BF$_4$	12.9	12.8 [30] 12.9 [23] 13.6 [27]
C_4C_1im BF$_4$	9.7	11.2 [33] 11.7 [30] 12.2 [69] 13.9 [24] 14.1 [27]
C_2C_1im NTf$_2$	13.8	12.0 [24] 12.3 [29] 12.3 [27] 14.0 [26]
C_3C_1im NTf$_2$	9.3	11.8 [23] 13.3 [24]
C_4C_1im NTf$_2$	9.3	11.5 [29] 11.6 [23] 14.0 [24] 15.0 [13] 13.7 [27]
C_2C_1im N(CN)$_2$	12.5	11.7 [13]
C_4C_1im N(CN)$_2$	10.3	11.3 [69]
C_6C_1im PF$_6$	7.1	8.9 [30] 15.5 [27]
N_{HHH2} NO$_3$	25.4	26.2 [23] 26.3 [24]
S_{222} NTf$_2$	14.0	13.2 [32] 15.8 [24]
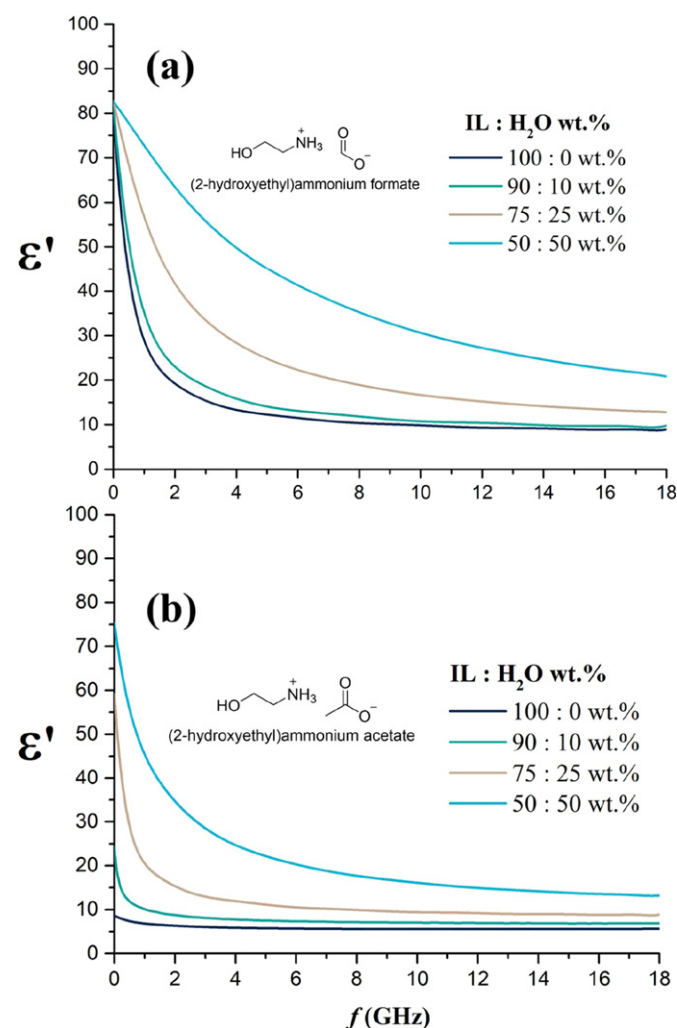
Fig. 9. The effect of increasing H_2O concentration on the complex permittivity spectra of (a) $N_{HHH(2OH)}$ HCO$_2$ and (b) $N_{HHH(2OH)}$ CH$_3$CO$_2$.

The most common route for IL synthesis (especially the well-researched imidazoliums) is via a metathesis reaction involving a halide salt precursor. This can result in trace halides remaining in the final ILs which cannot be removed by treatment at elevated temperatures and reduced pressures. Halide content of ILs has been shown to have an effect on the physicochemical properties, e.g. increasing viscosity and decreasing density [70]. In order to determine whether residual halide content affects IL complex permittivities, we prepared and measured C_2C_1im NTf_2 with varying concentrations of halide (< 50 ppm, 250 ppm and 500 ppm). No change in the complex permittivity was observed, even when an extreme excess was added. Residual water content and temperature have much more significant effects on the complex permittivity and these should be of primary concern when measuring the dielectric constant of ILs or when applied to electronic devices exploiting permittivity. Several literature sources provide experimental methods for the quantitative halide determination of ILs, including microfluidic electrochemical devices and specialised capillary electrophoresis techniques [71–73].

4. Conclusions

A comprehensive comparison of permittivities was performed with common liquids and solvents, which have been well-defined in the literature from a multitude of sources, using the identical measurement and extrapolation procedure utilized for ILs in this study. Our data are in excellent agreement with the myriad of complex permittivity literature sources. The comparison of static permittivities for ILs between this study and the literature shows agreement ranging from excellent to poor. There are many factors for this disagreement, such as purity and age of samples, water content, the dielectric measurement technique used, the calibration procedure employed, and temperature sensitivity.

64 ILs were selected in this study. These include 28 imidazolium ILs which are the most commonly used and reported cations, paired with a wide variety of anions, and 11 ILs comprising a choline cation with mostly amino acid anions, which generally exhibit higher viscosities when compared to more common ILs and are of interest to those exploiting green chemistry materials or when bio-compatibility is desirable. A sulfonium, 8 phosphonium and 9 ammonium cations were also chosen as these represent a significant portion of the other commonly available ILs classes. Finally, 8 pyrrolidinium, pyridinium and piperidinium ILs were included as these can form a wide variety of useful low-viscosity liquids and are easily synthetically customizable. We feel that the selected ILs represent a wide range of common and lesser known materials that exhibit a variety of thermal, physicochemical, bio-compatible and electromagnetic properties.

The frequency-dependent dielectric constants of all 64 ILs were found to be within the range 3–30 (with the exception of $N_{HHH(2OH)}$ HCO_2) with most following a known general trend of dielectric relaxation when approaching higher frequencies. This relaxation is reversed, albeit to a limited degree, when considering the ILs C_6C_1im I and C_8C_1im Cl. The slight increase in the dielectric constant from 0 to 18 GHz (of 0.5 for C_6C_1im I and 1 for C_8C_1im Cl) may result from the presence of single halide anions (I^- or Cl^-) which are present in both materials and will be investigated further. Another general observed trend throughout all the series is the reduction in overall permittivity when the mass or alkyl chain length is increased. This feature is best visualized through the imidazolium and choline series (Figs. 6 and 8). Fig. 7 shows the effect that functionalization of the 2-position of imidazolium cations has on polarity. Thus, addition of a methyl group to this position does not significantly reduce ε' for $C_4C_1C_1im$ NTf_2 compared to C_4C_1im NTf_2. In relation to the imaginary contributions of the complex permittivity spectra, it can be said that ILs with high electrical conductivities have large imaginary parts, which is in accordance with the literature for these inherently linked properties [74].

We have also shown that the dielectric constants of ILs can be rather sensitive to the concentration of water and maintaining water content

as low as possible is necessary for accurate measurement. This could be a reason for the previously reported high static values for the ILs $N_{HHH(2OH)}$ acetate/lactate [24,25]. We also determined that residual halides in the ILs examined does not affect the observed complex permittivity.

From the full range of ILs and their relative complex permittivity spectra (available in the supplementary data), it may be possible to select liquid materials with desired requirements. ILs with more stable dielectric relaxations across the full frequency range have also been identified, i.e. C_6py BF_4 or ILs with multiple large alkyl groups such as $P_{666(14)}$ Cl. This phosphonium chloride IL ($P_{666(14)}$ Cl) has other beneficial properties such as a temperature-stable complex permittivity and a wide liquid range (−69.8 °C to 350 °C), ideal for applications that require extreme temperatures and stable dielectric performance [75,76]. It has recently been exploited by our groups as the resonating material in a miniaturised ultra-wideband DRA, the first example of an ionic liquid RF device [5]. If one's requirements involve a more conductive medium, ILs with large imaginary contributions may be considered; these include C_2C_1im $N(CN)_2$, S_{222} NTf_2 and N_{HHH2} NO_3.

The presented complex permittivities, in combination with other reported physicochemical/thermophysical IL data, such as viscosity, density, conductivity, heat capacity and phase transition temperatures, can be of great use when selecting an IL with specific properties. In particular, the availability of a wide range of data will inform the application of ILs in catalysis, separation, electronics or perhaps a more comprehensive description of solvent properties.

Author contributions

J.X. and Y.H supervised the project. E.L.B synthesized and characterized the materials. E.L.B and C.S. carried out the permittivity measurements and analysed the data. E.L.B. prepared the manuscript, E.L.B., C.S., Y.H. and J.X. finalized the paper. All authors have read the manuscript.

Declaration of competing interest

The authors declare no conflict of interests here.

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Abbreviations[2]

CNT	carbon nanotube
IL	ionic liquid
DC	direct current
RTIL	room-temperature ionic liquid
MOF	metal-organic framework
DRA	dielectric resonator antenna
VNA	variable network analyser
PTFE	polytetrafluoroethylene
DMSO	dimethyl sulfoxide
MeOH	methanol
EtOH	ethanol
NPL	national physical laboratory
PCF	polynomial curve fitting
AA	amino acid
DIMCARB	dimethylammonium dimethylcarbamate
NHC	N-heterocyclic carbene
[Ch]	choline

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[2] All ionic liquid abbreviations can be found in the supplementary data file (Appendix A).

PIL   protic ionic liquid
EE   electronic engineering.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2019.111571 and includes: General Information, Materials, Permittivity Measurement Set-up/Procedure, Structures, Names, Abbreviations, Synthetic Procedures, Characterisation Data, Relative Complex Permittivity Spectra.

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