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Correlation of Dielectric Properties with Structure and H-Bonding for Liquids

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ABSTRACT: A study focused on the correlation among dielectric properties, molecular structure, and H-bonding is presented using liquid formamides with increasing carbon chain lengths as a model series. ^{1}H NMR is used to determine the extent of H-bonding via Abraham solute hydrogen bond acidity parameter, A. The results show a clear quantitative correlation, with higher A linked with increased relaxation times (τ) and a drop in the static dielectric constants (ε_s), with differences between the 1 and 2° amides observed. Overall, the findings advance our understanding of the intricate relationship between dielectric properties and H-bonding, with potential applications toward the design of materials exhibiting tailored dielectric properties and the study of amide-containing molecules (such as DNA, peptides, proteins, and nylon polymers) and other liquids which may associate via H-bonding.
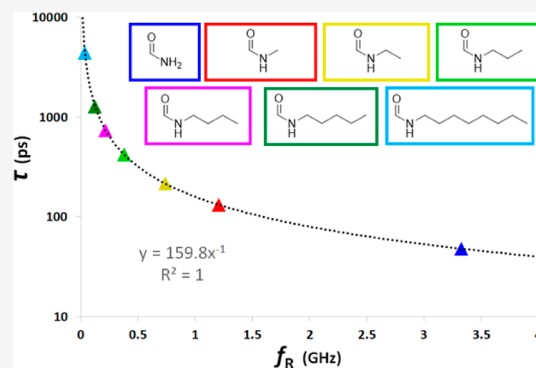
1. INTRODUCTION

Dielectric materials are used in many electrical and electronic devices and systems, and one of the most important performance indicators is complex permittivity. In most applications (such as capacitors, resonators, dielectric energy storage devices, and flexible electronics),[1,2] a low loss and stable permittivity are required, while in other applications (such as microwave absorbers), high-loss materials are required.[3]

Frequency-dependent permittivity (relative complex permittivity) can provide useful material information relating to polarity, conductivity, dielectric loss, ionic/dipolar relaxations, and atomic/electronic resonances and can be used to investigate factors such as intermolecular interactions, viscosity, formulation (in mixtures or composites), and purity.[4] Instruments that can measure dielectric properties are constantly improving, and it is now possible to measure solids, liquids, and composites over a broad frequency band using small sample sizes and nondestructive spectroscopy (see the Experimental Methods for details).

Dielectric relaxation information can be useful for a wide range of research areas, such as dielectric microwave-assisted heating, which has now become an established procedure in synthetic chemistry.[5] When studying the inter- or intramolecular interactions of a substance (e.g., H-bonding) detailed dielectric relaxation data can provide useful information on how these interactions affect the properties of a material.[6,7] In electronic engineering, microwave absorbing materials (MAMs) are a well-established and growing area of interest in both civil and military applications, with their absorbing properties based predominantly on the dielectric

relaxation and loss tangents of materials or composites.[8] MAMs have found significant relevance in energy harvesting, microwave darkrooms, stealth materials, and electromagnetic interference (EMI) technologies. With the rapidly increasing civil uses of radio frequency devices, EMI may now even have implications toward human health. With the number and power of electromagnetic wave communication devices in development growing, we require an increased understanding and ability to control the dielectric and relaxation properties of a huge variety of materials, mixtures, and composites, which will no doubt lead to many interesting applications.[9] Some of our recent work describes how preparing composite materials which possess H-bonding increases the dielectric relaxation over a broad frequency range, and how application of these composites can enhance antenna bandwidth performance, a novel approach in materials chemistry, and electronic engineering.[10]

The static dielectric constants (ε_s) of molecular liquids which associate via H-bonding have been found to be much higher than expected,[11] and attempts to explain these unusually high ε_s values using computational methods are available in the literature.[12] The effect of H-bonding on the dielectric relaxation of liquids and mixtures has also been investigated,
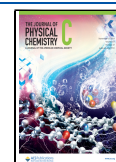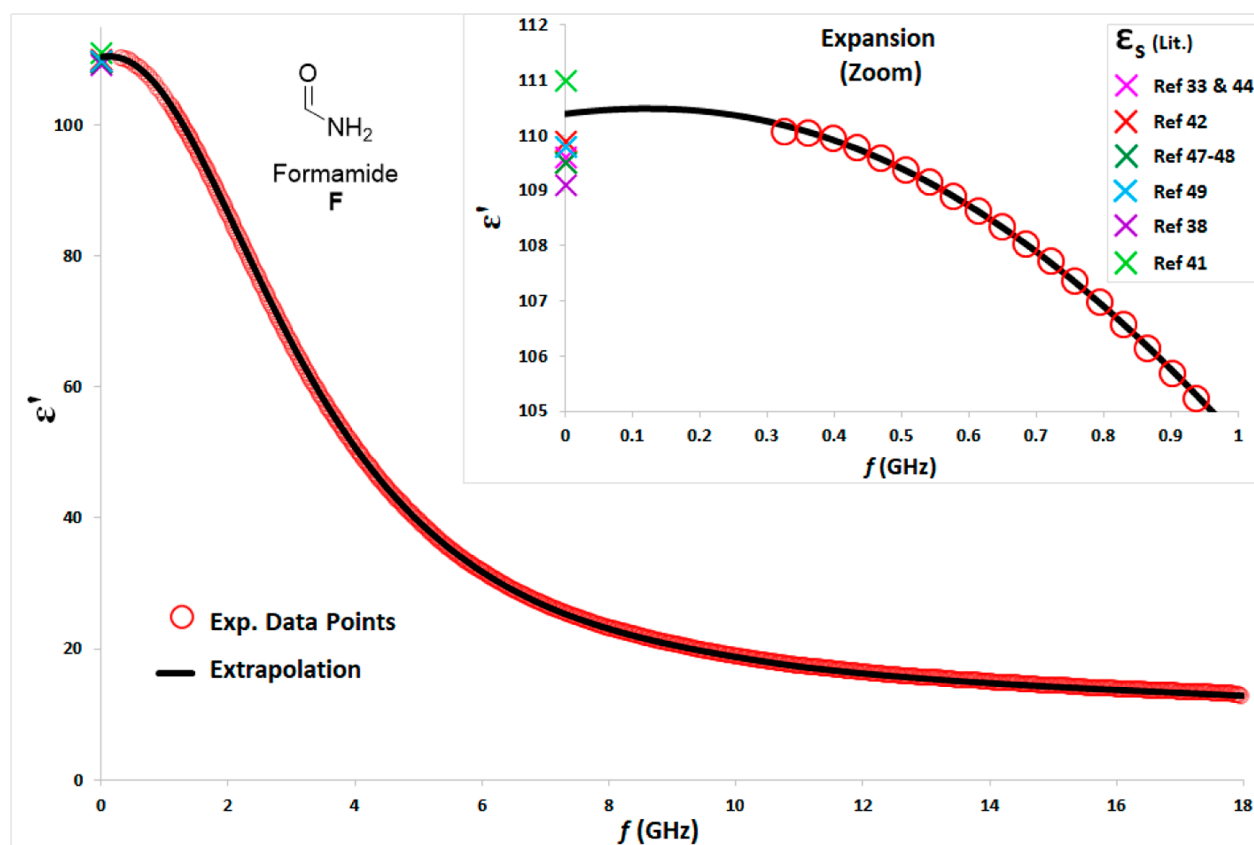
Figure 1. Example extrapolation for determination of the static dielectric constant (ε_s) with formamide (F). Literature values for static permittivity are shown as crosses.[33,38-49]

often using time-domain reflectometry, which is a useful technique for high-frequency measurements.[13-15] Petong et al. investigated the dielectric relaxation of H-bonded liquids (ethanol and hexanol), and their findings interestingly suggested that intermolecular interactions between the aliphatic groups play a significant role in the dynamics of the molecular reorientations.[16] A study involving glycerol and amide/amine mixtures demonstrated how using simple additive equations to approximate static and infinite permittivity values would lead to erroneous results, and that H-bonding was likely the cause of this variation.[17] Strong H-bonding interactions of amide−amide mixtures were also found to affect the static dielectric constant values deviation from mole-fraction mixture laws.[18] Shinde et al. used an estimation of the average number of H-bonds in combinations of 1,3-propanediol and 1,4-dioxane to explain the dielectric constant behavior of their mixtures,[19] and a recent study by Kutus et al. explored how differences in H-bonding interactions found in isotopes of water ($H_2^{16}O$, $D_2^{16}O$, and $H_2^{18}O$) result in variation of their dielectric relaxation spectra.[20]

In 2018, a study exploring the isopermitive frequency (IPF, defined as the frequency at which the relative permittivity of water is almost independent of temperature) investigated how the presence of ions (using NaCl/MgCl$_2$) can alter the H-bonding networks in water. This low-frequency technique (1−40 MHz) obtained qualitative information about the H-bond networks in water solutions and their rearrangements.[21]
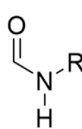
A combination of spectroscopic techniques has also proven useful when studying the heteromolecular H-bonding interactions between a mixture of nitrogen-based acceptors (amides/amines) and oxygen-based donors (alcohols, carboxylic acids, and water).[22] The presence, together with conformational analysis, of the H-bonds in mixtures of dimethylacetamide−butanol, aniline−isobutanol, cyanoacetamide−water, and N-methylpyrrolidone−glycerol was confirmed using a combination of dielectric spectroscopy and FTIR.[23-26]

NMR methods have also been used in combination with dielectric and other spectroscopic techniques (e.g., UV−vis) to deduce the presence of complex H-bond clusters in mixtures of donor/acceptor molecules. Kinart used ^1H NMR shifts in mixtures of high and low permittivity solvents to attempt to explain how H-bonding can affect the static dielectric constants of mixtures, although they were "not able to propose a model of such internal structure and further studies are clearly needed here".[27] A combination of ^{13}C NMR and dielectric measurements has also been used to reveal the formation of H-bonds between the mixtures of carboxylic acids and dioxane.[28,29] Impendence spectroscopy has been applied to the strongly H-bonded liquid amides N-methylpropionamide and N-ethylacetamide with orientational entropy effects quantified.[30]

Among polar organic molecules, amides possess a high degree of H-bonding, strong polarity,[31] and a wide liquid range and are easily synthetically customized. Amides are ubiquitous in nature and technology; they are the most prevalent structures found in biomolecules (e.g., peptides, proteins, DNA, and RNA) and hugely important in industrial plastics (e.g., nylons and Kevlar). The high static dielectric constants of amide molecules were even being investigated over 100 years ago.[11,32] Formamides have also been selected as a model systems for peptides, and their dielectric relaxations were

Table 1. Structures, Names, and Dielectric Data for a Series of Formamides at 298 K[a]

Structure	R	Name (Abbreviation)	MW	ε_s (exp)	ε_s (Lit.)	ε_∞ (exp)	ε_∞ (Lit.)	Relaxation Strength $\Delta\varepsilon$ ($\varepsilon_s - \varepsilon_\infty$)	Relaxation Frequency f_R (GHz)	Relaxation time τ (ps)
	-H	Formamide (**F**)	45.04	110.4	108.2 - 111.0	12.8	5.7 - 11.7	97.6	3.3	48
	-CH$_3$	*N*-Methylformamide (**NMF**)	59.07	189.1	173.5 - 189.0	8.3	3.4 - 7.9	180.8	1.2	132
	-CH$_2$CH$_3$	*N*-Ethylformamide (**NEF**)	73.10	102.4	101.5 - 102.7	5.4	N/A	97.0	0.74	216
	-(CH$_2$)$_2$CH$_3$	*N*-Propylformamide (**NPF**)	87.12	89.7	N/A	4.7	N/A	85.0	0.38	421
	-(CH$_2$)$_3$CH$_3$	*N*-Butylformamide (**NBF**)	101.15	78.9	N/A	4.0	N/A	74.9	0.22	737
	-(CH$_2$)$_4$CH$_3$	*N*-Pentylformamide (**NPnF**)	115.18	66.4	N/A	3.6	N/A	62.8	0.13	1263
	-(CH$_2$)$_7$CH$_3$	*N*-Octylformamide (**NOF**)	157.26	35.0	N/A	3.0	N/A	32.0	0.036	4421

[a]All samples were synthesized or obtained commercially (see Experimental Methods & Supporting Information), dried over activated molecular sieves, and stored under N$_2$(g) prior to use. All measurements were performed at 298 K, unless otherwise stated. ε_s and ε_∞ literature values for F,[18,33,38−49] NMF[18,33,38,41,43,44,46,48−52], and NEF.[49−51]

studied, with the average numbers of monomers in the chains of H-bonded NMF molecules deduced.[33] Molecular dynamics simulations have been utilized to explore the similarity of H-bonded networks in liquid formamide and water, focusing on the static dielectric constants.[34] Due to their H-bonding ability, polarity, high dielectric constants,[12,35,36] and relaxation in the microwave region, formamides were selected as a model series for this study. Herein, we present complex permittivity data for a series of formamides with varying carbon chain lengths and correlate the data with chemical structure and H-bonding interactions/strength. Information regarding complex permittivity—structure relationships will be useful for a wide variety of scientific disciplines and technologies, ranging from electronic devices, biochemistry, industrial plastics, and physical organic chemistry concerning the complex phenomena of strong H-bonding interactions.

2. EXPERIMENTAL METHODS

2.1. Dielectric Measurement. The relative complex permittivities of the liquids/materials presented in this paper were measured using an Agilent N9917A FieldFox Microwave Network Analyzer and a Keysight 85070E Dielectric Probe Kit.[37] The measurement frequency range of the instrument was set from 30 kHz to 18 GHz with 1001 data points. A three-point calibration method was employed, which comprised open-circuit, short-circuit, and distilled water measurements. All measurements were conducted at room temperature (298 K unless otherwise stated). The liquid samples were dried over activated molecular sieves, stored under N$_2$(g) prior to use, and held using borosilicate glass vials with PTFE-lined caps. The probe was immersed into the liquid samples at a depth of 10 mm from the surface of the liquids. The relative complex permittivities of the compounds, including the real and imaginary parts, were measured accordingly. We also repeated the calibration and measurement steps multiple times to ensure the repeatability of data. Compounds with well-defined relative complex permittivity spectra found in the literature were measured after each calibration to ensure the reliability of results. Supporting measurements and calibration data were also performed independently at the National Physical Laboratory (NPL). Additional measurements were performed using the dielectric assessment kit for thin layers (DAK-TL2) from SPEAG (Schmid & Partner Engineering AG, Switzerland), which is capable of measuring both liquid and solid samples.

Static permittivities (ε_s) were extrapolated from the lowest measured point, which is set to 30 kHz but can vary from material to material. Available static values from the literature

were also used to confirm measurement accuracy; an example extrapolation is given in Figure 1 for formamide (F), and additional extrapolation examples with literature comparisons can be found in the Supporting Information (Figures S1 and S2). Infinite permittivity (ε_∞) is the value obtained from the highest possible measurement frequency (18 GHz). Relaxation frequency (f_R) is defined as the frequency at which the imaginary part is maximum. Relaxation time (τ) was determined using the formula $\tau = 1/2\pi f_R$.

2.2. Materials and Synthesis. Full synthetic and analytical information on the preparation and purification of amides used in this study is available in the Supporting Information. Full imaginary spectra for the formamide series up to 18 GHz can be found in the Supporting Information. Table 1 presents the dielectric data measured for a series of formamides with varying carbon chain lengths.

3. RESULTS AND DISCUSSION

Figure 2 shows the real parts of the permittivity spectra for a series of formamides with increasing carbon chain lengths,
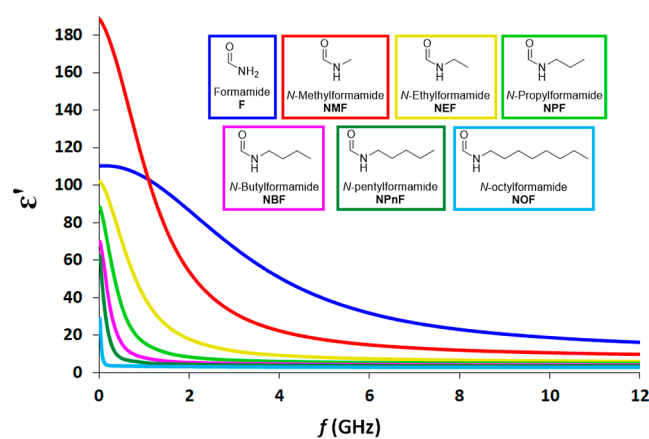

Figure 2. Real parts of complex permittivities for a series of formamides.

ranging from F (C0) to NOF (C8). Measurements were performed up to a frequency of 18 GHz, but the scales in Figure 2 have been adjusted for clarity. An apparent trend in the dielectric constant and relaxation is visible, especially when considering only the 2° amides NMF, NEF, NPF, NBF, NPnF, and NOF. The differences in the dielectric behavior between 1, 2, and 3° amides can be correlated with the potential for H-bonding and will be discussed later. As the carbon chain length increases from methyl to octyl (i.e., NMF to NOF), there is a

drop in ε_s and an increase in sharpness of relaxation, which coincides with a lower relaxation frequency (f_R) and faster relaxation time (τ). The same trend can be observed when examining the relaxation strength $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$), which ranges from 180.8 (NMF) to 32.0 (NOF).

This difference in complex permittivity can be attributed to the larger molecular weight and the speed at which amides with larger carbon chains can reorient with increasing speed of the electric field as the frequency increases. An amide with a methyl group (C1—NMF) can reorient more easily in sync with the changing electric field at a higher frequency than an amide with an octyl group (C8—NOF).

3.1. H-Bonding in 1, 2, and 3° Amides. H-bonding has been previously identified as a key factor affecting the dielectric properties. It can contribute toward deviations in expected static dielectric constants, dielectric relaxation, and the variation of dielectric properties from ideal mixing laws within mixtures of liquids (see Introduction on previous literature). Figure 3 shows the real parts of the complex permittivities for
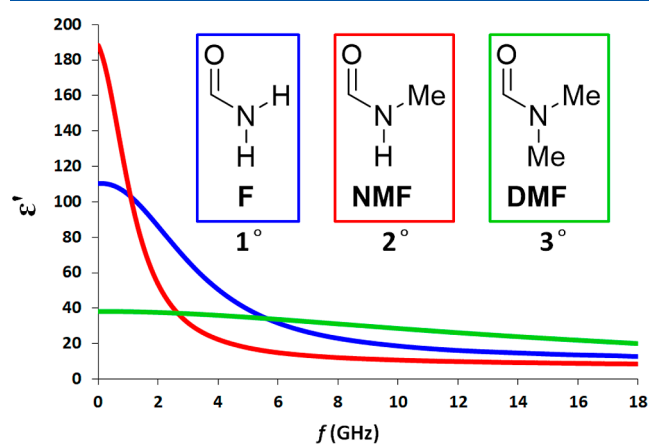

Figure 3. Real parts of the complex permittivity spectra for F, NMF, and DMF.

three related amides: F, NMF, and DMF (real and imaginary parts of the complex permittivity spectra for DMF can be found in the Supporting Information, Figures S4 and S5). This series represents 1, 2, and 3° amides, respectively, essentially differing only by the addition of methyl groups ($-CH_3$). The dipole moment of a molecule is often a good indicator of what ε_s might be. However, there are other important contributions which can greatly affect the dielectric constants/complex permittivities and in this trio of amides those appear to be prevalent. The dipole moments of F, NMF, and DMF are very similar (3.73, 3.83, and 3.82 D, respectively),[49] and so, there must be another factor determining the different ε_s's and relaxation profiles as seen in Figure 3.

If we consider the intermolecular H-bonding contributions within this selection of simple amides, we can begin to understand the difference in complex permittivity spectra. The greater the extent of H-bonding in a liquid, the sharper the dielectric relaxation will be.[16] This is due to the competing processes of the dipoles attempting to reorient in time with the changing field (giving high permittivity), and these rotational motions being slowed down by the intermolecular forces, in this case, H-bonding, leading to a drop in permittivity (therefore increasing the relaxation).

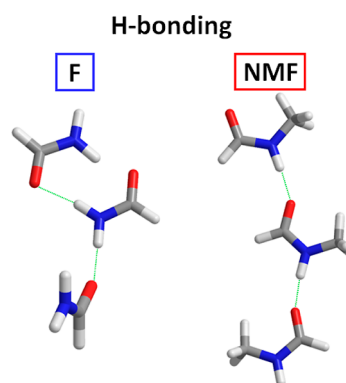F is an 1° amide, meaning it can H-bond in two different directions (Figure 4F) forming ring-like configurations.

Figure 4. Directional H-bonding contributions in F and NMF.

Although we see increased permittivity compared to DMF (and its subsequent drop, i.e., relaxation), the bonding directions can partially cancel each other out.[53] NMF is a 2° amide, with H-bonding now possible in a more linear chain-like direction (Figure 4—NMF). The ring- or chain-like H-bonding configurations for F and NMF, respectively, are similar to those found in the analogous pair of molecules, acetamide, and N-methylacetamide, which have been confirmed with simulation.[53] This directional bonding influence appears to greatly increase the polarity ($\varepsilon_s = 189.1$) but also makes NMF more susceptible to an increase in the speed of the changing electric field, i.e., the drop in permittivity is sharper and faster than in F; therefore, dielectric relaxation is greater. The 3° amide DMF cannot H-bond intermolecularly as it only has an acceptor group, and its complex permittivity is primarily determined by the intrinsic polarity of the molecule itself and not by H-bonding; it, therefore, exhibits the lowest permittivity and relaxation in this series.

3.2. Correlation—Structure versus Dielectric Properties. A correlation was observed within the formamide series, which consists of seven liquids with carbons increasing in a linear fashion, from F (C0) to NOF (C8). Figure 5 plots relaxation time (τ) versus carbon chain length, and a trend is clearly apparent, fitted by a polynomial function. The same correlation was also observed in series of ionic liquids with increasing molecular weights and is likely ubiquitous across related liquid materials.[4]

From Figure 5, it is now possible to predict the relaxation time (τ) in picoseconds for materials not prepared or measured. For instance, a formamide containing a C6 chain (N-hexylformamide—NHF) would have a $\tau \approx 2008$ ps and a formamide containing a C10 group (N-decylformamide—NDF) would have a $\tau \approx 8385$ ps. It is also possible to plot carbon chain length (or molecular weight) versus ε_s and ε_∞, therefore predicting these values for unknown materials within a series (additional correlation figures can be found in the Supporting Information, Figures S9–S14).

To determine whether structural isomers may have an effect on the dielectric properties, N-tert-butylformamide (NtBF) was measured. Figures S6–S8 present the complex permittivity spectra (real and imaginary parts) and relaxation time (τ) vs carbon chain length correlation graph for NtBF. Figure S8 shows that there is still a good fit with the correlation trend for the isomer NtBF, specifically compared to NBF. Additional amide isomers should be prepared and measured to fully investigate how carbon chain configurations affect the dielectric properties.
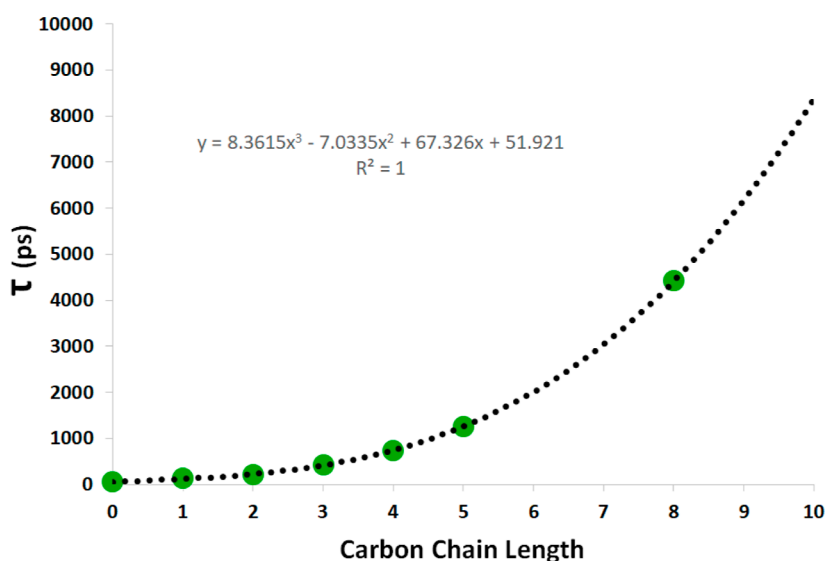
Figure 5. Relaxation time (τ in ps) versus carbon chain length for the formamide series (green circles) from F (C0) to NOF (C8).

3.3. Correlation—H-Bonding versus Dielectric Properties. As discussed previously in relation to primary, secondary, and tertiary amides, H-bonding has a powerful effect on complex permittivity, specifically the static dielectric constant and subsequent relaxation. Calculating the H-bonding characteristics of a system is complex and generally achieved using DFT calculations involving various sized clusters of molecules which can be time-consuming and requires expert knowledge and computational skills.[54] However, Abraham et al. have developed a simple and facile NMR method for the determination of the overall, or summation, of the H-bonding extent of a liquid. It is achieved through obtaining ^{1}H NMR spectra in both CDCl$_3$ and DMSO-d_6 deuterated solvents and subsequently calculating the chemical shift in ppm of the −NH or −OH signals relative to a tetramethylsilane (TMS) standard.[55,56] The observed shifts can then be used to calculate the Abraham solute hydrogen bond acidity parameter, A, using eqs 1 and 2. The formamide series were measured using the NMR method, and both $\delta\Delta$ and A are presented in Table 2.

$$\delta\Delta = \delta(\text{DMSO}) - \delta(\text{CDCl}_3) \tag{1}$$

$$A = 0.0065 + 0.133\delta\Delta \tag{2}$$

Figure 6 plots the Abraham hydrogen bond parameter, A, versus relaxation frequency (f_R). The data have a good fit

Table 2. NMR-Derived Shifts, Abraham Solute Hydrogen Bond Acidity Parameters (A), FT-IR C=O Stretches, and Kirkwood—Fröhlich Correlation Factors (g_k) for a Series of Formamides

name/abbreviation	$\delta\Delta$	A	C=O stretch (cm^{-1})	g_k
formamide (**F**)	1.37	0.19	1663.2	1.83
N-methylformamide (**NMF**)	1.87	0.26	1653.9	4.47
N-ethylformamide (**NEF**)	2.14	0.29	1656.4	3.26
N-propylformamide (**NPF**)	2.17	0.30	1656.7	N/A
N-butylformamide (**NBF**)	2.30	0.31	1657.2	N/A
N-pentylformamide (**NPnF**)	2.37	0.32	1657.9	N/A
N-octylformamide (**NOF**)	2.43	0.33	1660.3	N/A

using a polynomial function and show how H-bonding extent (described by increasing A) results in dielectric relaxation at lower frequencies (Figures 2 and 6). Figure 6 (and eq 3) also allows for the determination of f_R values from A. Figure 7 presents the correlation between the relaxation frequency (f_R) and relaxation time (τ) in picoseconds, now describing how H-bonding results in increased dielectric relaxation. It is possible to extract τ values using eq 4, which are obtained from the fit in Figure 7.

It is also possible to determine τ from A in one step using eq 5 (a combined form of eqs 3 and 4). Figure 8 then correlates τ with permittivity parameters, in this example showing the real parts, from which we can derive the static and infinite permittivity values ε_s and ε_∞, which is also possible via eqs 5 and 6.

Additional correlation figures between dielectric properties, chemical structure, and H-bonding can be found in the Supporting Information (Figures S9−S14).

$$f_R = 86.079A^2 - 68.465A + 13.229 \tag{3}$$

$$\tau = \frac{159.8}{f_R} \tag{4}$$

$$\tau = \frac{159.8}{86.079A^2 - 68.465A + 13.299} \tag{5}$$

$$\tau = \frac{10^7}{\varepsilon_s^{2.221}} \tag{6}$$

$$\tau = \frac{46894}{\varepsilon_\infty^{2.828}} \tag{7}$$

Starting from simple ^{1}H NMR measurements, $\delta\Delta$ and A can be easily obtained, which then allows for direct determination of dielectric properties (f_R, τ, ε_s, and ε_∞) using Figures 6−8 and/or eqs 3−7. It is also possible to input these values into dielectric relaxation models, such as the Debye model, or modified versions of the Debye model including the Cole−Cole, Havriliak−Negami, and Davidson−Cole relaxation models.[57] Figure S17 shows how this procedure can be used to simulate full complex permittivity spectra, starting from only
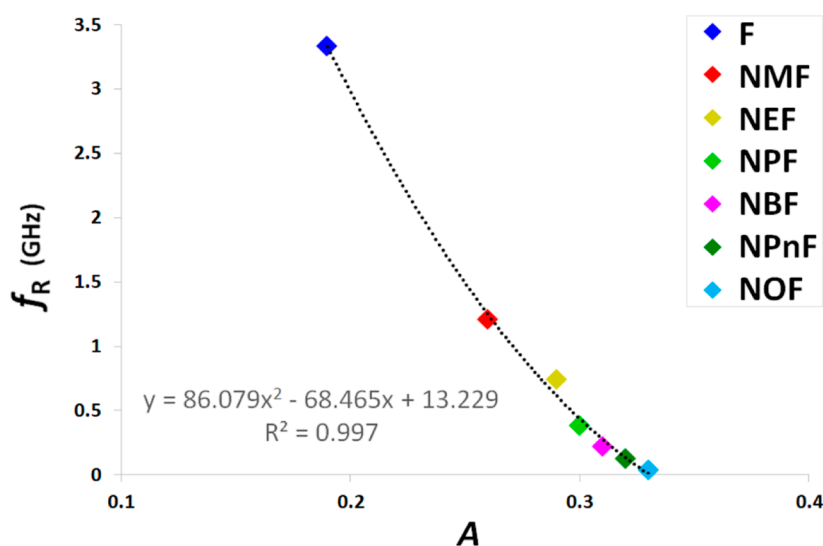
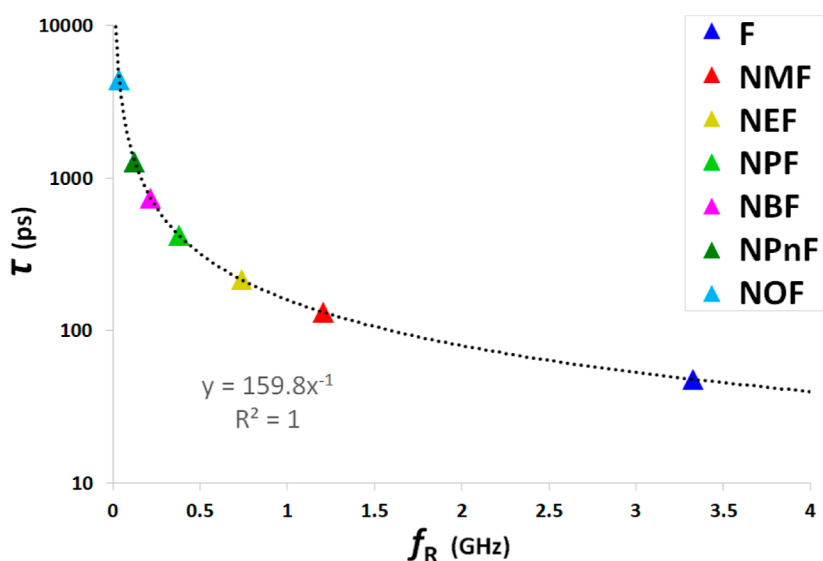**Figure 6.** Relaxation frequency (f_R in GHz) vs hydrogen bond parameter (A).

Figure 7. Relaxation time (τ in ps) vs relaxation frequency (f_R in GHz).

NMR measurements, with good agreement between experiment and simulation. Figure S17 assumes a Debye type relaxation for the amide NPnF, although any models can be used depending on the type of molecule being simulated.

It is also possible to plot loss tangent ($\tan \delta$) spectra across the desired bandwidth using the real and imaginary parts generated using the above method and/or simulated complex permittivity spectra (Figure S15). The loss tangent is obtained by the equation $\tan \delta = \varepsilon''/\varepsilon'$. These data would be highly relevant for researchers performing chemical reactions under microwave-assisted heating or for electronic engineering applications where $\tan \delta$ is a key property. Although many models exist for the prediction of dielectric relaxation, the estimation of $\tan \delta$ is a much more challenging task, with few accurate examples in the literature. Utilizing measurement data (e.g., NMR) and H-bonding levels to improve the accuracy of $\tan \delta$ predictions could be a very promising route.

When H-bonding involves amide carbonyl functional groups (C=O), the wavenumber of the carbonyl stretching vibration, accessible via FT-IR, is sensitive to differences in the H-bond interactions. H-bonding can affect the electron density distribution around the carbonyl group, altering the bond strength and vibrational frequency of the C=O stretching mode. An additional correlation was observed when the FT-IR spectra of this series of formamides were analyzed with increasing alkyl chain lengths. Table 2 presents the C=O stretching vibrations of the amide groups in wavenumbers (cm^{-1}). The FT-IR spectra were obtained from pure liquids, which were dried thoroughly over molecular sieves. The Supporting Information Figures S15 and S16 present correlations between the FT-IR C=O peak shifts, the number of carbons in the alkyl chain, and the Abraham H-bond parameter A. Similar to the correlations observed between the dielectric properties and Abraham parameter A, formamide, the only primary amide, differs from the remaining secondary amide series. The trend from C1 to C8 (i.e., NMF to NOF) then progresses with an increasing blue shift in the C=O peak position (cm^{-1}) as the carbon chain (or A) increases, which is accurately fitted by a polynomial function.
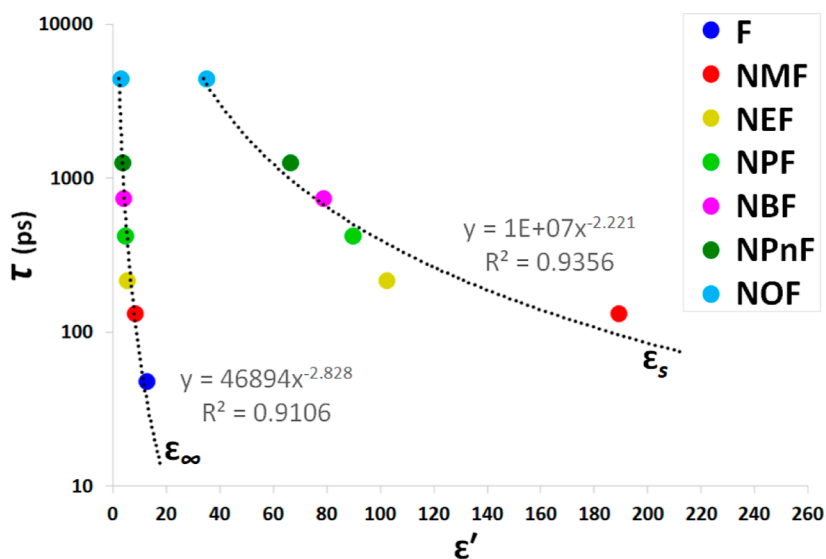
Figure 8. Relaxation time (τ in ps) vs permittivity (ε') showing both static and infinite permittivity values (ε_s & ε_∞).

As suggested in Figures 3 and 4, the directionality of the H-bonding network can have a pronounced effect on the dielectric properties, even when the dipole moments are similar. The Kirkwood–Fröhlich correlation factor (g_k) was then applied in order to examine this model amide series, the details of which can be found in the Supporting Information (page S13). The Kirkwood–Fröhlich equation uses various parameters, such as ε_∞ and the molecular dipole moment (μ), and data in the literature were only available for the more common liquids F, NMF, and NEF. Table 2 presents g_k values for the formamides with available data found in the literature, and again another correlation is apparent. As the Dannhauser model suggests, high values for the cross-correlation ($g_k > 1$) indicate more chain-like organization, and lower values for cross-correlation ($g_k < 1$) indicate more ring-like H-bond formations between neighboring molecules.[58−61] The lower g_k value for F, compared to the much higher values for NMF and NEF, further supports the ring/chain-like H-bond networks observed in the 1 and 2° amides, respectively. This is in agreement with a simulation-based investigation into the analogous pair of acetamide and N-methylacetamide,[53] the difference in permittivity spectra between F, NMF, and DMF (Figure 3), and the correlations observed either using the previous NMR or FT-IR methods.

4. CONCLUSIONS

In summary, broadband dielectric spectroscopy was used to investigate a model series of formamides with increasing carbon chain lengths from C0 (F) to C8 (NOF). As the carbon chain length increases, there is a noticeable and clear trend of decreasing static dielectric constants (ε_s) and relaxation frequency (f_R), while simultaneously, increasing relaxation times (τ) are observed. The different possible H-bonding directions in 1 and 2° amides are found to influence the static dielectric values (ε_s), presumably due to the formation of either ring-like or more linear chain-like H-bonded networks. An isomeric example is found to not deviate from the apparent trend and can be seen in the Supporting Information.

Using the Abraham ¹H NMR method for evaluation of the summation of H-bonding within a system, a strong correlation

is observed between increasing the H-bond extent and the dielectric properties f_R, τ, ε_s, and ε_∞. Extraction of these dielectric properties derived from ¹H NMR values can allow for simulated full complex permittivity spectra when they are applied to dielectric relaxation models. This trend is additionally supported by correlations between the C=O peak shifts (FT-IR) with increasing alkyl chain lengths and the Kirkwood–Fröhlich correlation factor, which further supports the observed differences between 1 and 2° hydrogen bond networks.

Thus, using indirect and readily accessible methods for the determination of a system's complex permittivity profile, without the requirement for complicated instrumentation, calibrations, or vector network analyzers, could be a useful approach to investigating the dielectric properties of liquids/materials.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c03484.

Extrapolation for static dielectric constant with DMF; extrapolation for static dielectric constant with NMF; imaginary parts of complex permittivity of formamides; real part of complex permittivity of DMF; imaginary part of complex permittivity of DMF; real part of complex permittivity of NtBF; imaginary part of complex permittivity of NtBF; relaxation time vs chain length of formamides; correlation of static permittivity vs carbon chain length of formamides; correlation of infinite permittivity vs carbon chain length of formamides; correlation of relaxation time vs relaxation frequency of formamides; correlation of NMR derived shift vs carbon chain length of formamides; correlation of relaxation frequency vs NMR-derived shift of formamides; correlation of FT-IR C=O stretching vibration vs carbon chain length of formamides; correlation of FT-IR C=O stretching vibration vs hydrogen bond parameter; and full complex permittivity spectra for NPnF (PDF)

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Notes

The authors declare no competing financial interest.

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