Nuclear Magnetic Relaxation Mapping of Spin Relaxation in Electrically Stressed Glycerol

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ABSTRACT: This work discusses nuclear magnetic relaxation effects in glycerol subject to a strong electric field. The methods used are 1.5 T magnetic resonance imaging (MRI), referenced by 9.4 T nuclear magnetic resonance (NMR). While MRI allows a glycerol probe to be sampled with a high voltage (HV) of 16 kV applied to the probe, NMR provides precise molecular data from the sample, but the sample cannot be tested under HV. Using MRI, the recording of magnetic relaxation times was possible while HV was applied to the glycerol. NMR spectroscopy was used to confirm that MRI provides a reasonably accurate estimation of temperature. The applied HV was observed to have a negligible effect on the spin–lattice relaxation time $T_1$, which represents the energy release to the thermal bath or system enthalpy. In contrast to that, the spin–spin relaxation time $T_2$, which does represent the local entropy of the system, shows a lower response to temperature while the liquid is electrically stressed. These observations point toward a proton population in electrically stressed glycerol that is more mobile than that found in the bulk, an observation that is in agreement with previously published results for water.

1. INTRODUCTION

The electrohydrodynamics (EHDs) of polar liquids exposed to strong electric fields (up to $\sim 10^6$ V m$^{-1}$) have been studied extensively. Hertz$^1$ was one of the first to note the rotational motion in liquid–solid dielectric systems, Quincke$^2$ observed that the interfacial tension between two fluids was changed by the application of an external electric field and a subsequent exertion of forces on the fluid body inducing rotational motion, and Armstrong$^3$ discovered the so-called “floating water bridge” in 1893. The floating water bridge is a horizontal EHD bridge forming between two beakers filled with deionized water when a high direct current (DC) voltage is applied. The experimental configuration allows proton conduction and diffusion processes to occur as would normally occur while the liquid is exposed to air under ambient conditions while also reducing the possibility of a dielectric breakdown induced by the applied potential.

Recently, a phase transition in electrically stressed liquid water was reported, whereby the breakdown of rotational symmetry in the molecular dipole results in a dipole polarization current, which propagates along the hydrogen bond network. The emergence of the novel phase is described using quantum field theory demonstrating that electric fields of this magnitude generate nontrivial material transitions.$^4,5$ While these experiments were performed in deionized water without any EHD flow or free charge carriers, the horizontal EHD bridges offer the possibility to test the influence of electric fields on polar liquids under more relevant conditions for engineering or biology. In these aqueous bridges, an increased positive surface charge was found, leading to a decrease in surface tension by app. 4%.$^6,7$

The question now arises whether and how electric fields of such strength can alter physical properties in liquids made of polar molecules other than water. Nonaqueous liquid bridges have been previously investigated for other polar molecules, namely, methanol, ethanol, 1-propanol, 2-propanol, glycerol, and dimethyl sulfoxide (DMSO).$^8,9,10,11$ In DMSO, an aprotic liquid, ionized molecules like $\text{O}_2$ are suggested to act as charge carriers,$^{11}$ whereas in protic liquids, e.g., water, protons have been identified to fulfill this purpose. The alcohol group protons in glycerol are expected to behave in a similar fashion to those in water, which were found to be more delocalized and more mobile in electrically stressed water than in bulk.

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water. In this work, the enhanced delocalization of protons in electrically stressed glycerol is investigated by nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) in terms of spin–spin relaxation time ($T_2$) and spin–lattice relaxation time ($T_1$) measurements.

This was done for three reasons:

1. The $T_2$ relaxation time of glycerol (~53 ms) is much shorter than that of water (~2700 ms) at 1.5 T used for MRI\(^{15}\) such that the acquisition times for relaxation time measurements can be shortened.

2. The higher viscosity of glycerol (1.412 Pa s)\(^{15}\) than of water (8.9 $\times$ 10\(^{-4}\) Pa s)\(^{16}\) potentially reduces the influence of motion artifacts on the resulting relaxation time maps.

3. Upon dissociation of protons from hydroxyl groups (OH groups), the remaining glycerol backbone contains additional distinguishable alkyl protons, which allow a separate NMR spectroscopic analysis of these moieties.

NMR spectroscopy is a common tool for molecular structure and dynamics analysis\(^2\) and can serve in the present study as a benchmark for the MRI recordings of operating glycerol bridges. Therefore, the objective of this study is to test the hypothesis that moderately strong electric fields have an influence on the properties of polar protic molecules other than water.

2. BACKGROUND

2.1. Electrohydrodynamic Bridges in Polar Liquids.

The fluid motion in an electrically stressed liquid composed of polar molecules is governed by the laws of both hydrodynamics and electrodynamics whose combination is referred to as electrohydrodynamics or electro-fluid-dynamics.\(^{18,19}\) In this approach, an additional term enters the Bernoulli equation for an electrically stressed, adiabatic, and incompressible liquid, the so-called Maxwell pressure. When the HV applied to the liquid is large enough, this EHD pressure may counteract the hydrostatic pressure, so that an electrically stressed polar liquid moves upward, against gravity.\(^{20}\)

Experiments with EHD bridges were performed for several decades\(^2\),\(^{12}\) but only recently, a century-old experiment in electrically stressed water has been rediscovered.\(^{23}\) First proposed by Lord Armstrong in 1893,\(^3\) this experiment presents a horizontal EHD bridge, often referred to as the floating water bridge. The electrochemistry of such a horizontal EHD liquid water bridge has been investigated\(^24\) describing the bridge as a protonic semiconducting liquid. Generated in the anolyte by HV electrolysis, protons are transported to the catholyte through the water bridge, which acts as an Ohmic resistor limiting the current in this HV experiment. In the bridge, the protons cause a nonthermic infrared (IR) emission.\(^25\) If the bridge is broken abruptly, the system is taken out of its electrochemical equilibrium, and excess protons and $\alpha$-protons (proton holes in the liquid) remain in the beakers, producing charged water with altered physical properties relevant for engineering, such a reduced surface tension as previously mentioned.\(^6\) Details about how to safely build and run an EHD bridge setup are discussed elsewhere.\(^26\)

Horizontal aqueous EHD bridges have recently provided insights into the molecular physics of electrically stressed water because these bridges are both large and stable enough to be used in experiments that access the molecular length scale and also require a macroscopic sample volume, e.g., radiation scattering\(^{27–31}\) and spectroscopy.\(^{33,34}\) Previous Raman studies reported a small fraction of molecules in electrically stressed water to be dynamically polarized,\(^35\)\(^,\)\(^36\) a state where the $\text{O}−\text{H}$ vibrations quantum-mechanically couple and hydrogen bonds are strengthened.\(^35\)\(^,\)\(^36\)

2.2. Magnetic Resonance Principles Used in the Present Study.

NMR spectroscopy is an analytical method to investigate the electronic environment of individual atomic nuclei as well as their interactions with atomic nuclei of adjacent atoms. It enables structure elucidation of molecules and investigation of molecular dynamics behavior. The method is based on magnetic nuclear resonance, a resonant interaction between the magnetic moment of atomic nuclei located in a strong static magnetic field, with a high frequency electromagnetic irradiation. Only these isotopes are detectable, which have a nonzero nuclear spin in the ground state and thus possess a magnetic moment ($\mu$).

In simple words, such atomic nuclei are charge carriers possessing a rotating nuclear spin. Their magnetic moment ($\mu$) can assume only certain quantum-mechanically defined orientations in an external magnetic field. The number of possible orientations is determined by the nuclear spin quantum number $I$. For each nuclear spin quantum number $I$, there are $2I + 1$ orientations and each orientation is assigned a magnetic nuclear spin quantum number $I_m$. Protons (in hydrogen atoms) that have $I = \frac{1}{2}$, consequently, result in two discrete energy states. Without an external magnetic field, the states are energetically equal, energy differences arise in the presence of an external magnetic field caused by the Zeeman effect.

Nuclear resonance phenomena are based on the excitation of nuclear spin transitions between different $m_I$ The required energy $\Delta E$ is proportional to the strength of the external magnetic field $B_0$ and to the magnetogricy ratio $\gamma$ of the considered atomic nuclei

$$\Delta E = \gamma hB_0 = h\omega_L.$$  

This energy is irradiated as resonant electromagnetic waves with the resonance frequency $\omega_L$, which is called Larmor frequency. The resonant frequencies are influenced by individual small magnetic fields, which are generated by the influence of the electronic environment around an atomic nucleus or by interaction with adjacent atomic nuclei in the same molecule. This leads to slightly different resonance frequencies $\omega_I$ of atoms in different positions in a molecule. A descriptive, more comprehensive, and detailed explanation of general magnetic resonance principles can be found elsewhere.\(^{17,34}\)

The slightly varying Larmor resonance frequencies $\omega_I$ of different atoms in a molecule lead to different resonance lines in the resulting NMR measurements. Since all molecules of a given chemical component have essentially the same structure, these different resonance lines add up and can be detected as separated signals and signal groups in the resulting NMR spectrum. They are normally indicated by relative frequency differences between a signal of certain nuclei in the investigated molecule ($\nu_{sample}$) and those of a nucleus in a standard ($\nu_{std}$). These differences are assigned as chemical shifts $\delta$, whereas the reference is assigned to a chemical shift of zero. The chemical shifts $\delta$ are calculated according to...
The recovery follows exponential behavior described by

\[
\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}
\]

(3)

The \(T_1\) time describes the disappearance of the transverse magnetization \(M_z\) and \(M_0\) according to the Bloch equations.\(^{35}\) Within this process appears the loss of phase coherence between spatial neighboring spins, which for hydrogen carrying liquids and solution includes not only intramolecular modes but also local intermolecular modes. \(T_2\) is named spin–spin relaxation time as it is an adiabatic process whereby energy is redistributed locally but without the whole spin system losing energy. This provides a representation of the local entropy of the spin system. The recovery follows exponential behavior described by

\[
\frac{dM_z}{dt} = \frac{-M_z}{T_2}
\]

(4)

The subatomic origin of the relaxation processes is the interaction between the excited spins and their environment, in particular with a magnetic gradient field induced by molecular motions of surrounding other spins. These spins, e.g., from other nuclei or unpaired electrons, cause an additional local magnetic field that oscillates in time through Brownian motion and the rotation of the molecules. The most important interaction mechanism for the nuclei with \(I = \frac{1}{2}\) is the magnetic dipole–dipole interaction. Spectral components at the resonance frequency allow transitions and thus lead to the relaxation of the previously excited nuclei. In the case of a Brownian motion of the molecules, the resulting time-independent autocorrelation function can be set by an exponential decay with the correlation time \(\tau_c\). The solution of the Fourier transformation of this function is called spectral density function \(J(\omega)\)

\[
J(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}
\]

(6)

This equation represents the distribution of nuclei possessing different correlation times \(\tau_c\). Figure 1a shows the schematic function for five different molecular mobilities, triggered for example by different sample temperatures. It should be noted that at a given frequency corresponding to the Larmor frequency \(\omega_L\), there is a temperature at which a maximal number of nuclei have this frequency.

In Figure 1b, the number of respective nuclei with Larmor frequency \(\omega_L\) is plotted against the molecular tumbling rate (reciprocal of the correlation time \(\tau_c\)). For the \(T_1\) time, an extremum is easily detectable, in which the relaxation time has a minimum (solid line). The position of this extremum depends on the Larmor frequency \(\omega_L\) and thus on the applied external magnetic field \(B_0\). The dotted line shows the course for a larger \(B_0\) and a consequently higher \(\omega_L\). This is to be considered within investigations of the temperature dependence of \(T_1\) relaxation times at different magnetic field strengths \(B_0\) in NMR and MRI. The \(T_2\) time shows a different behavior at lower temperatures and tumbling rates (dashed line). Molecular interactions, such as aggregate formation, strongly

\[
\delta = (\nu_{\text{sample}} - \nu_{\text{ref}}) \times 10^6 / \nu_{\text{ref}}
\]

(2)

They are hence independent of the spectrometer magnetic field strength \(B_0\) and given in parts per million (ppm) in order to allow assignment and identification of the nuclei using the chemical shift (\(\delta\)). This powerful tool of varying chemical shifts is most commonly used for structure determination and can also provide information about the interaction between two (different) molecules.

Apart from chemical shift \(\delta\), two further observables are primarily investigated in the present research, namely, \(T_1\) and \(T_2\) relaxation times. The \(T_1\) relaxation is understood in NMR spectroscopy and MRI to be a process that causes nuclear spin magnetization to return to its equilibrium state after excitation. The \(T_2\) relaxation takes place through the desynchronization of the spins within the coherence plane. These effects are based on two relaxation mechanisms, which are described by the relaxation times \(T_1\) and \(T_2\) and are caused by different magnetization components. The \(T_1\) time is derived from the recovery of the full magnitude into the direction \(M_z\) according to the Bloch equations.\(^{35}\) It is called spin–lattice relaxation time as the absorbed energy is redistributed to the thermal bath providing a measure of the enthalpy of the system. The recovery follows exponential behavior described by

\[
\frac{dM_z}{dt} = -\frac{M_z}{T_2}
\]

(5)
favor transitions in transverse magnetization ($M_x$ and $M_y$), resulting in faster $T_2$ relaxation and thus shorter $T_2$ times. Further detailed explanations of chemical shifts and relaxation phenomena can be found elsewhere.17,34

3. MATERIALS AND METHODS

3.1. MRI Imaging of Glycerol Electrohydrodynamic Bridges in the Magnetic Field Environment. 3.1.1. Sample Preparation. Electrohydrodynamic bridges in glycerol were prepared in a manner consistent with the method described previously for studies in water36 using nonmagnetic materials in the construction of the fixating armature, cable supports, and electrode mounts. The glass beaker diameter was 30 mm, and the beaker spouts were left in contact throughout the measurements for higher stability and to avoid bridge rupture, liquid leakage, and electrical arcing in the setup – all of which could pose a hazard to the MRI scanner. Such a bridge extended over 4 mm from the anode side to the cathode side beaker but was always supported by glass. These types of bridges behave in a manner consistent with horizontal aqueous EHD bridges (see the characteristic of EHD bridges8).

MRI of the glycerol bridges was performed on a 1.5 T scanner at a resonance radio frequency (RF, Larmor frequency) of 63.70 MHz (Magnetom Sonata, Siemens Healthcare, Erlangen, Germany) using a standard circular-polarized knee coil. The experimental setup is illustrated in Figure 2. The glycerol bridge was aligned so that the long axis of the bridge was parallel to the main magnetic field $B_0$ with the anode placed toward the foot end of the patient table and the cathode toward the head end. The bridge center was located in the isocenter in the head–feet direction, in the right–left direction, and some millimeters above the isocenter in the anterior–posterior direction.

A plastic box filled with 500 mL of agar and covered with a glass plate formed the electrically insulating support base for the beakers. The agar phantom was used as a signal reference for intensity normalization. All materials were fixed in place using MR compatible tape, which does not produce artifacts in the recorded images. Platinum foil (99.999% Pt, MaTeck GmbH, Jülich, Germany) was soldered to both the HV and ground leads with wires that are sufficiently long (≈10 m) to reach from the experiment at the MR scanner isocenter to the power supply located just outside the room via an RF suppressing pass-through in the Faraday cage wall.

3.1.2. $T_1$ and $T_2$ Relaxation Time Measurements. The bridges studied for this section were prepared from anhydrous glycerol (49767-100ML, Lot # BCBK7056V, Sigma Life Science, St. Louis, MO, USA). A total of 31 pairs of $T_1$ and $T_2$ time measurements were made using data collected from nine glycerol bridges operated at 16 kV and 10–20 μA. Five regions-of-interest (ROIs) in the glycerol bridge were chosen for determination of magnetic relaxation times, with ROI 5 recording the bridge section, ROIs 3 and 4 the spout sections, and ROIs 1 and 2 the beaker sections, all shown in Figure 3.

Glycerol temperature was measured before and after bridge operation in both the anode and cathode beaker with an alcohol thermometer. The typical temperature rise in the beakers during two complete measurement series (requiring ~1 h) was 1.5 ± 0.5 °C.

Thermographic recordings done in a separate study8 with glycerol bridges operated at 0.3 W clearly show that the glycerol warms during bridge operation. Since the EHD bridge acts as an Ohmic resistor, most of the heating is localized to the bridge itself. Because temperature monitoring inside was not feasible inside the MR coil, temperatures were estimated outside the MRI scanner and without air cooling usually present in the test section of MRI scanners. Direct probe measurements were performed using fiber optic temperature probes (OTG-Q, Opsens, Québec, Canada).

Before applying HV to the glycerol setup, an isotropic three-dimensional spoiled fast low-angle shot (FLASH) sequence covering the experimental setup was employed to optimize and fix the sagittal imaging plane visualizing beakers and the glycerol bridge. Estimation of relaxation times in these regions was based on two-dimensional spin echo measurements in this plane. For $T_1$ estimation, spin echo sequences with two different repetition times ($T_R$) were acquired with the following protocol parameters: $T_E$, 70 and 300 ms; echo time ($T_E$), 8 ms; bandwidth, 170 Hz/pixel; field-of-view, 150 ×
For $T_2$ estimation, a multiecho spin echo sequence with 16 different echo times (8.3/16.6/24.9/33.2/41.5/49.8/58.1/66.4/74.7/83.0/91.3/99.6/107.9/116.2/124.5/132.8 ms) was used. For each pair of spin echo images (with different $T_2$ times) and each multiecho spin echo measurement, average relaxation times were estimated in both spin echo images with di erent echo times (8.3/16.6/24.9/33.2/41.5/49.8/58.1/66.4/74.7/83.0/91.3/99.6/107.9/116.2/124.5/132.8 ms) was used. Further protocol parameters were as follows: $T_E$, 400 ms; bandwidth, 280 Hz/pixel; field-of-view, 150 × 150 mm$^2$; resolution, 0.8 × 0.8 × 3.0 mm$^3$; number of averages, 3; imaging time, 3 min 54 s. To compensate for a decreased signal-to-noise ratio in the images during the existence of the bridge, measurements for $T_1$ determination were three-fold averaged and measurements for $T_2$ determination six-fold, with correspondingly longer imaging times.

For each pair of spin echo images (with different $T_2$ times) and each multiecho spin echo measurement, average relaxation times were estimated in five ROIs in both beakers, near the spouts or bridge base, and in the bridge itself (Figure 3). In both spin echo images with different $T_E$, mean ROI signal intensities were derived from ROIs drawn as similar as possible but carefully excluding electronic noise artifacts and partial volume areas in the time-varying bridge. Mean $T_1$ times at the five localizations were determined from fitting the mean signal intensities of corresponding ROI pairs to the spin echo signal intensity equation:

$$\text{signal intensity} = A(1 - 2e^{(-T_E-T)/T_1} + e^{-t_E/T_1})$$  \hspace{1cm} (7)\text{where A and (mean) } T_1 \text{ are the fitting constants. Fitting was performed using the statistical analysis software package NCSS.}$$

For $T_2$ estimation, the image with the lowest echo time ($T_E = 8.3$ ms) and images with predominant noise contribution (typically $T_E > 83$ ms) were excluded from the series of multiecho spin echo images. Pixel signal intensities of the remaining multiecho spin echo images were linearly fitted to the logarithm of the signal intensity equation:

$$\text{signal intensity} = Ae^{-T_E/T_1}$$  \hspace{1cm} (8)\text{to determine } T_2 \text{ of the pixel (and an additional fitting constant A). This calculation was performed for any pixel by the scanner software (syngo VA2S, Siemens Healthcare, Erlangen, Germany) to produce a } T_2\text{-map. Mean } T_2 \text{ values in both beakers, at both beakers’ spouts, and in the bridge were determined from corresponding ROIs.}$

3.1.3. Temperature Calibration Measurements. In order to perform relaxation-based thermometry, a calibration standard was imaged and processed using the same methods as described for the bridge. The temperature calibration sample was a bottle of glycerol immersed in a water bath held in an insulating box. The measurements were performed twice, once with an open bottle of glycerol and once with a sealed bottle of anhydrous glycerol. A thermocouple recorded the temperature of the sample, which was allowed to equilibrate between temperature steps. A diagram of the setup is shown in Figure 4.

3.1.4. Single-Voxel Spectroscopy in the MRI Scanner. For the recording of single-voxel proton spectra in the MRI, a tube (1 cm diameter) filled with glycerol was equipped with a cathode and anode. Parameters of the employed STEAM (stimulated echo acquisition method) sequence were as follows: $T_E$, 1300 ms; $T_D$, 20 ms; mixing time ($T_M$), 10 ms; voxel size, 10 × 10 × 25 mm$^3$; number of averages, 350; imaging time, 7 min 35 s. The measurements were taken from a region between the electrodes. Spectra were recorded without electrical voltage and under a voltage of 3.5 kV. The RF was fixed to the resonance frequency of the proton in H$_2$O. Processing of the spectra was performed by the standard scanner software.

3.2. High-Field Nuclear Magnetic Resonance Spectroscopy of Glycerol. 3.2.1. Sample Preparation. To obtain a sample for high-field NMR measurement, glycerol has been used, without an electric field applied to the sample. The amount of water from humidity was in the same range as in the glycerol used for the MRI measurements. The glycerol was filled into 5 mm high-precision NMR sample tubes (Wilmad 507 PP 8”, Armar AG, Dottingen, Switzerland). A C$_6$D$_6$ vortex capillary was added to the probes to avoid mixtures between the deuterated substance used for the lock and the investigated liquids. Comparable systems have been described earlier.

3.2.2. Nuclear Magnetic Resonance Spectroscopy. All spectra were recorded on a DRX-400 AVANCE spectrometer (Bruker, Rheinstetten, Germany) with a two channel z-gradient inverse probe head using the bundled software Topspin 1.3 (Bruker, Rheinstetten, Germany). Irradiation and measurement frequency in a field strength of 9.4 T was 400.13 MHz for protons (1H). Temperature was adjusted in the range between 27 and 55 °C with an accuracy of ±0.05 °C. The NMR tube was rotated during the measurements with 20 rps. For all measurements, the residual C$_2$D$_6$H in not fully deuterated C$_2$D$_6$ in the vortex capillary was used as external reference ($\delta_H = 7.15$ ppm). One-dimensional proton (1H) spectra were recorded with a H-pulse flip angle of 30°, acquisition of 64k data points, and a relaxation delay of 1.0 s. Free induction decays (FID) of eight...
scans were added for one spectrum. The summed FID was directly Fourier transformed to gain spectra with a spectral range of 8000 Hz.

$T_1$ time constants for different groups of protons were determined by the inversion recovery method changing the recovery delays in 12 steps from 10.0 ms to 8.0 s (0.01/0.1/0.2/0.3/0.5/0.7/1.0/1.5/2.0/3.0/4.0/8.0 s). For each scan, a $180^\circ$ pulse, the recovery delay, and a $90^\circ$ pulse were followed by the acquisition. During acquisition, 32k data points were collected and the subsequent relaxation delay took 5.0 s. FIDs resulting from eight scans were added prior to Fourier transformation, which led to the spectra with a spectral range of 6000 Hz. Signal intensity was determined by integration. The $T_1$ times were calculated using the software Topspin 4.0.5 (Bruker, Rheinstetten, Germany).

The $T_2$ time constants for different groups of protons were measured with the spin echo sequence (CPMG) using a $\tau$ of 10.0 ms and varying the number of spin echo blocks ($2 \times \tau$-times) from 2 to 50 in 12 steps resulting in times of 0.04/0.08/0.16/0.24/0.4/0.8/1.4/2.2/3.2/4.4/6.0/10.0 s. For each scan, a $90^\circ$ pulse was followed by the series of spin echo blocks ($\tau$ - $180^\circ$ pulse - $\tau$) prior to the acquisition. During acquisition, 32k data points were collected and the subsequent relaxation delay took 5.0 s. FIDs resulting from eight scans were added prior to Fourier transformation, which led to the spectra with a spectral range of 6000 Hz. Signal intensity was determined by integration. The $T_2$ times were determined manually using the software Topspin 4.0.5 (Bruker, Rheinstetten, Germany) and considering the intrinsic line over the signal intensity with respect to intensity change caused by scalar $^1$H−$^1$H coupling during the delay times.

4. RESULTS AND DISCUSSION

4.1. Nuclear Magnetic Resonance Spectroscopy. For a better understanding of the data recorded by MRI, $^1$H NMR spectra as well as $T_1$ and $T_2$ times of glycerol were sampled in the NMR spectrometer at 9.4 T without an electric field applied to the liquid.

The proton ($^1$H) NMR spectrum of anhydrous glycerol is shown in Figure 5 for a temperature of 27 °C and a Larmor frequency of 400 MHz. Three groups of resonance peaks with six peaks altogether caused by the 10 protons in glycerol and water are clearly identifiable in Figure 5. In detail, a multiplet of partly overlapping signals from the carbon bound protons ($\delta_H = 3.68$ (CH); $\delta_H = 3.55$ (CH$_2$ $2 \times a)$); $\delta_H = 3.48$ (CH$_2$ $2 \times a'$)) are visible in Figure 5. The latter mentioned signal is caused by a small amount of water, which is always present in glycerol due to its hygroscopicity and sample preparation in open air – a situation comparable to the open-air measurements in the MRI.

The line widths at half-height of all signals are in the range of ca. 5−10 Hz. This is quite large compared to standard $^1$H NMR measurements showing line widths at half-height in the range of ca. 1−2 Hz. Such broad lines are caused by relatively fast nuclear spin relaxation. Rather slow chemical exchange of the free protons furthermore causes the separation of the proton signals of the two different types of hydroxyl groups and water. With rising temperature, the molecular movement and chemical exchange are enhanced. These effects cause narrowing of the line width at half-height for proton signals due to increasing relaxation times. However, concomitant faster chemical exchange of the oxygen-bound protons (R−OH and H$_2$O) leads to coalescence of their signals. Hence, for alcohols and water, the three signals merge toward one broad signal with increasing temperature, whereas the fine splitting of the carbon-bound protons becomes more pronounced (data not shown). However, within the investigated temperature range, all protons lead to separated signals, which allow individual determination of $T_1$ and $T_2$ times for all nuclei in nearly all measurements.

Figure 5. $^1$H NMR spectrum of glycerol at 27 °C with peak assignments as indicated in the molecular structure. The integrals give the relative abundance of the protons. Water content can thus be determined to be about 5% (mol/mol), which corresponds to about 1% (w/w). The numbers underneath the plot provide the integral values for each signal group.
Values of $T_1$ and $T_2$ relaxation times in glycerol at varying temperatures (27 to 55 °C) are plotted in Figure 6. $T_1$ times of the protons in OH groups and water increase with temperature (Figure 6a). This behavior indicates that the molecular motion of these temporarily dissociated protons leads to correlation times, which tend to a branch known as the extreme narrowing limit, which appears on the right side in Figure 6a. In contrast, all carbon-bound protons, which are indicated in red in Figure 6a, show minimum $T_1$ times at about 42 °C. This extremum indicates that these molecular moieties have a maximal relaxation for the 400 MHz Larmor frequency used.45 In contrast, $T_2$ times of the protons in OH groups and water change only slightly in the investigated temperature range, although coalescence and concomitant increasing $T_1$ times indicate changes in their tumbling rates. However, $T_2$ times of all these protons are rather small in the measured temperature range. This indicates that they make a major contribution to spin–spin relaxation of entire glycerol. Possible
temperature-dependent changes in these $T_2$ times are only moderate, indicating relatively small variations in their tumbling rate. However, measurement of these temperature dependent changes is not very accurate due to the signal broadening caused by coalescence. Thus, it is not possible to make a precise statement about relatively small changes in the $T_2$ times in this temperature and relaxation time interval.

**4.2. Single-Voxel Spectroscopy in an Electric Field.**

Since the EHD setup was too large to be placed in a high-field NMR spectrometer at 9.4 T, $^1$H NMR spectroscopic measurements of glycerol were performed in the 1.5 T MRI scanner using the stimulated echo acquisition mode sequence (STEAM). A spectrum recorded without electrical HV is shown in Figure 7a. Here, all signals are shifted about 1.5 ppm compared to those in the $^1$H NMR measurement discussed in the previous section (Figure 5), which is caused by referencing to different standards (eq 2). The signals of protons from OH groups and $H_2O$ can be seen at app. 6.5 ppm, and signals from alkyl protons are at app. 5.0 ppm. Due to the comparatively poor spectral resolution compared to the NMR measurements, the signals of these two signal groups each overlap and thus both coincide into undissolved signal groups. In contrast to the signal intensities of the NMR measurement (Figure 5), in the MRI measurement, the signals of protons from OH groups and $H_2O$ have a much larger signal intensity than signals from alkyl protons.

These differences in signal intensity between $^1$H NMR spectra recorded in NMR and single-voxel spectroscopy in MRI are very likely caused by three different reasons: On the one hand, the relaxation times of the nuclei are significantly different, as can be seen in Figure 6. Within $T_M$ and $T_E$ of the STEAM sequence, this leads to a different rate of reduction in signal intensity of the two signal groups. Furthermore, there is a development of homonuclear coupling between the alkyl protons during these times. This leads to the formation of signal forms with dispersion components in the signal group of the alkyl protons. Due to the low digital resolution, the resulting signal shape is not exactly represented and consequently leads to a significantly reduced intensity of the signal group. This effect is explained and discussed in detail elsewhere. A third reason can be a low amplitude and limited bandwidth of the RF in the MRI scanner, by which the two signal groups are stimulated to different degrees. This would be comparable to selective excitation in high-field proton NMR measurements in principle. A close examination of which of these three effects is responsible to which extent for the different intensities of the two signal groups in the single-voxel spectroscopy in the 1.5 T MRI scanner has not been carried out.

The spectrum shown in Figure 7b presents the single-voxel $^1$H spectrum under a voltage of 3.5 kV. Interestingly, the chemical shifts of all protons do not significantly differ between the two measurements with and without HV excitation of glycerol. Hence, for the discussion in the next sections, it can be stated that any influence on the chemical shift from the HV electric field applied to the glycerol bridge setup (Figures 2 and 3) can be neglected. This is correct both for frequency differences between the signal groups as well as between the signal groups and the Larmor frequency. Comparing Figure 7a,b, it is interesting to note that the signals of the protons from OH groups and $H_2O$ at about 6.5 ppm increase in amplitude and decrease in line width, although no unambiguous interpretation for that can be given from this measurement.

Comparing the spectra recorded by NMR (Figure 5) and MRI (Figure 7), some general conclusions can be drawn concerning the use of MRI. On the one hand, in MRI, the relaxation times are averaged over all proton signals in the entire frequency region. This is due to the fact that only a simultaneous excitation of the entire frequency range as well as a summed recording over all excited frequencies is possible. The varying proportion of signal intensity over all these proton
signals leads to contributions from different protons, which are not equivalent to their molar ratio in the molecule. Therefore, the proportion of OH protons and H$_2$O protons (signal at app. 6.5 ppm) is several times larger than that of the alkyl-bound protons (signal at app. 5.0 ppm) in the MRI spectra. For determination of $T_1$ times, this effect is less critical in the temperature range above 42 °C as their temperature dependence tends to be similar for all protons (Figure 6a). This is in particular correct for the measurements at 1.5 T as the extremum of the spectral density is shifted to lower tumbling rates (smaller $\tau_C^{-1}$) than measurements at 9.4 T (see Figure 1b). In the temperature-dependent changes of the $T_2$ times, however, in MRI, the over-represented $T_1$ times of the OH and H$_2$O protons show only small changes in the double-digit millisecond range (15−70 ms), while the contribution of the increasing $T_2$ times of alkyl protons with rising temperature is under-represented (compare Figure 6b). The difference cannot be exactly determined or corrected from the relative signal integrals in the spectra shown in Figure 7 as the chemical shift of the OH proton and H$_2$O proton signal itself is slightly temperature-dependent.

These results reveal that averaged $T_1$ relaxation times of glycerol recorded in an MRI scanner will tend to provide a reasonably accurate estimation of temperature as all nuclei behave in the same way in this temperature range. It has, however, to be noted that in MRI for $T_2$ time measurements, the relatively constant contribution of the OH protons is over-

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Figure 9. Comparison of $T_2$ on $T_1$ relaxation times taken from nine glycerol bridges. Relaxation times were extracted from five regions-of-interest (see Figure 3): (a) bulk anolyte (ROI 1 red squares), bulk catholyte (ROI 2 black squares), anode bridge base (ROI 3 red triangles), cathode bridge base (ROI 4 black triangles), and the bridge itself (ROI 5 black circles). Red indicates those data from the high-voltage (HV) beaker. Panel (a) plots the full dataset; panels (b−d) show the datasets for bulk, bridge base, and bridge, respectively. The glycerol EHD bridges were operated at 16 kV and 10−20 μA.
represented in the averaged $T_2$ time, while the more
temperature-dependent portion of the alkyl protons is
significantly under-represented due to their smaller contribu-
tion caused by a lower signal intensity. For further discussion,
it is important to note that this is true for measurements with
and without HV excitation.

4.3. Temperature Calibration of Relaxation Times of
Glycerol by Magnetic Resonance Imaging. Within the
temperature ranges of the calibration experiments of 22 to 83
°C, $T_1$ and $T_2$ relaxation times demonstrated an almost linear
relationship (determination coefficient $R^2 = 0.9955$ for the
open and $R^2 = 0.9813$ for the closed bottle, respectively).

Figure 8a represents the $T_2$ versus $T_1$ relaxation time plots
together with the linear regressions.

The temperature calibration measurement data for $T_1$ and
$T_2$ were fitted using a type of exponential function as given in

$$T_{1,2} = ae^{b(T-c)}$$

(9)

The fit coefficients $a$, $b$, and $c$ were derived using a nonlinear
regression in the statistical analysis software package NCSS.37

Figure 8b demonstrates the $T_1$ and $T_2$ time temperature
calibration curves of the experiment with glycerol open to the
atmosphere with $R^2$ values of 0.9988 and 0.9952 for $T_1$ and $T_2$,
respectively.
temperature in the beakers is about room temperature or of the material from this bridge section. For this reason, the heating of the liquid in the beakers is mainly due to transport experiments are shown in Figure 9. While Figure 9a plots show the results of all five evaluated ROIs, Figure 9b–d shows the datasets for bulk, bridge base, and bridge, respectively.

In the beakers (ROI 1 and ROI 2, Figure 9b), the determined values for the relaxation times have a relatively low spread and the entropy-related spin–spin relaxation time \( T_1 \) does follow the temperature rise in relation to the \( T_2 \) time approximately the same way it does in the bulk without an HV applied \( (R^2 = 0.2137 \text{ for ROI 1 and } R^2 = 0.4101 \text{ for ROI 2}) \). Since the EHD bridge acts as an Ohmic resistor, a main voltage drop of 16 kV applies to the short section between the onset of the bridge in the anode beaker (ROI 3) and the onset of the bridge in the cathode beaker (ROI 4) and not to the bulk in the beakers (compared also to aqueous EHD bridges'). The heating of the liquid in the beakers is mainly due to transport of the material from this bridge section. For this reason, the temperature in the beakers is about room temperature or slightly above (app. 25 °C with \( T_1 \) at 60 to 65 ms according to the calibration characteristic plotted in Figure 8b).

The spread in data is much larger in ROIs 3 and 4, where the bridge base forms in the anode and the cathode beakers (Figure 9c). Probe measurements revealed an average temperature rise of app. 8 °C, a little higher at the anode side, compared to the cathode side of the bridge (see Figure 3, 25–30 °C, \( T_1 \) app. 70 ms). When the temperature in these sections increases, the \( T_2 \) time no longer follows accordingly while the HV is applied to the liquid \( (R^2 = 0.1225 \text{ for ROI 3 and } R^2 = 0.0364 \text{ for ROI 4}) \).

The most pronounced spread can be found in the ROI 5 with an average temperature rise by 15 °C (35 °C, \( T_1 \) app. 80–85 ms). From the bridge section, the highest variations in relaxation time are reported; in this ROI, measurement artifacts are likely the cause. Even at low speed, fluid flow can transport signal out of the measurement volume and temperature fluctuations during measurement times will introduce nonlinearities in the relaxation dynamics, causing the strong variations in recording \( T_1 \) and \( T_2 \) times. However, similar to the cathode beaker’s bridge base, in average, there is nearly no change of \( T_2 \) observed in the bridge section \( (R^2 = 0.0021) \) for a broad range of \( T_1 \) times (between 60 and 120 ms, or 25 to 40 °C according to the calibration curves in Figure 8b).

In Figure 10, the same data are given as temperatures, with the temperatures derived from the calibrated relaxation times \( (T_1 \text{ as well as } T_2) \) for glycerol as shown in Figure 8b for the open beaker configuration without HV applied.

From the calibration curves plotted in Figure 8b, it is evident that in the temperature range discussed (shaded area in Figure 8b), the possibility to estimate temperatures by MRI is limited due to the low dependence of relaxation times on temperature and the large uncertainties in this temperature range. On the other hand, from Figure 9 and another publication, we learn that the glycerol in the beakers (ROIs 1 and 2) is not exposed to high electric fields, with temperature probe data available. Therefore, a calibration for the temperature offset was performed. For this temperature calibration, the thermocouple probe measurements in the beakers were used (see the Materials and Methods section). Since temperatures derived from \( T_1 \) in ROI 1 and ROI 2 already corresponded to the measured probe temperatures, only the temperatures calculated from \( T_2 \) had to be calibrated. Figure 10a plots the full dataset, while Figure 10b–d shows the datasets for bulk, bridge base, and bridge, respectively. Due to the calibration procedure, the probe temperature and the \( T_1 \) and \( T_2 \) temperatures have to match for Figure 10b.

When comparing the temperatures in the other bridge sections to the probe measurements (Figure 10c,d), it is evident that measurements derived from \( T_2 \) show a tendency to overestimate the temperature. There is no significant discrepancy between the anode and cathode sides, and in all thermocouple and IR thermography recordings, both have...
about the same temperature. Thus, the temperature derived from the $T_1$ time matches the probe recordings and those of previous thermographic recordings, but $T_2$ overestimates the temperatures for ROIs 3 to 5.

As for Figure 9, it must be mentioned that in the bridge ROI measurement artifacts are likely. Local variations in voltage density ($\nabla E \approx 10^{10} \text{ V} \cdot \text{m}^{-2}$) and different turbulent effects should be mentioned apart from local temperature variations.

The significance of the data is discussed in Figure 11 with the help of a Bland–Altman plot. In this plot, two different measurement procedures for the temperature are compared, each of which produced errors in measurement. While the data in the beakers are by definition in good correlation, the data from the bridge base and from the EHD bridge show a significant deviation in temperatures estimated from $T_1$ and $T_2$ times. In the EHD bridge, the voltage drop is highest (compared also to aqueous EHD bridges) and so is the data shift between temperatures derived from $T_1$ and from $T_2$ times.

4.5. Discussion of $T_1$ and $T_2$ Variations in Electrically Stressed Glycerol. A recalculation of measured $T_1$ and $T_2$ times to the present temperatures using the calibration curves from Figure 8 should lead to a linear progression as any temperature-dependent changes, e.g., changes of chemical shifts, are considered by experimental calibration curves. Hence, it is expected that the two derived temperatures will agree and should line up with the diagonal line in Figure 10. However, comparing $T_1$ and $T_2$ times measured in the EHD glycerol bridge clearly indicates that temperatures calculated from the $T_2$ times are slightly higher than the temperatures calculated from the $T_1$ times. Different changes of the chemical shifts of OH and alkyl protons caused by electrical voltage (3.5 kV) or flowing medium as well as concomitant changes in the excitation of the two proton species at high voltages cannot be held responsible as reasons for such deviations since such shift changes are marginal in EHD-driven glycerol (Figure 7).

Let us, hence, first assume that the applied electric field leads to a reduction of the averaged $T_1$ times and thus to incorrectly calculated temperatures. Such an influence cannot be ruled out, but in this experiment, such an effect is rather small since the temperatures from the $T_1$ times correspond to those measured by the probe (indicated by the cross in Figure 10). So, the results reveal that averaged $T_1$ relaxation times of glycerol will tend to provide a reasonably accurate estimation of temperature. It is therefore more likely that the $T_2$ times increase significantly due to the applied electric field (Figure 8b).

From a recent Raman study and previous studies using femtosecond mid-infrared pump-probe spectroscopy, we found that the electric field enhances proton conduction in EHD bridges made of water. Whenever an electric field is applied to a protic liquid, like glycerol, an increasing number of protons escape recombination as first discussed by Onsager and Brière. Under HV, the dissociation rate is proportional to the electric field magnitude, but the recombination rate is not. Such high electric fields can be found in the anode beaker enhancing the dissociation rate. The highest field gradients are found in the bridge and its bridge basis, which drives a proton current through the bridge.

At the molecular level, this results in an increased mobility of the dissociated (positively charged) protons. These are in equilibrium between the dissociated and OH group bound forms with exchange rates, which are faster than the measuring time of a free induction decay in MRI. The quite well resolved, narrow 1H signal of these protons at ca. 6.5 ppm in Figure 6b indicates this rapid exchange. Consequently, the entropy of these protons becomes much larger due to the influence of the electric field than enthalpic changes. In the region near the extreme narrowing limit, this enhanced exchange rate leads to a reduction in the number of OH protons that precess with the Larmor frequency. Consequently, the relaxation times ($T_1$ and $T_2$) of these protons should noticeably increase.

This change in the relaxation times is mainly caused by the influence of the electric field on proton mobility due to the design of the EHD glycerol bridge apparatus, with virtually no electric current. From previous investigations in electrically stressed water, we learned that when an HV is applied, such an increased proton mobility is caused by a dynamical coupling between the single molecule OH vibrations, leading to long-range phonon-like modes increasing proton conductivity. This quantum field effect drives the system out of thermal equilibrium and certainly will influence system entropy and spin–lattice relaxation in the way it is observed in Figures 9 and 10. The associated enthalpic effects (represented by the $T_1$ times) due to the heating and energy release to the thermal bath in all ROIs are represented by the calibration curves in Figure 8 and match quite well for MRI and NMR recordings. Hence, the influence of the electric field on the spin–lattice relaxation is small and the $T_1$ times are less affected.

Previously, we observed in an experiment with a free hanging glycerol bridge high velocities and fast fluctuations. We now understand that entropic effects will cause protons to be more mobile when glycerol is electrically stressed compared to glycerol in the bulk. As with water, this higher proton mobility and stronger delocalization might have an effect on the physical properties of electrically stressed glycerol.

5. Conclusions

In a recent work, the authors observed the emergence of a new population in electrically stressed water that supports polarization currents. In water, this leads to a higher proton mobility and surface charges, which in turn reduce surface tension.

In this work, another protonic liquid, glycerol, was tested under the influence of applied HV by 1.5 T MRI as well as at 9.4 T NMR with glycerol under no electric stress. NMR spectroscopy was used to confirm that MRI provides a reasonably accurate estimation of temperature. Under this premise, MRI enables the mapping of relative changes in $T_1$ and $T_2$ relaxation times when an HV is applied to the liquid, with the $T_1$ time providing a measure of the enthalpy of the system and the $T_2$ time representing the local entropy of the spin system.

When an HV is applied to glycerol, it turned out that associated effects in enthalpy are well represented by the temperature calibration curves recorded without HV applied, which correspond well for MRI and NMR recordings, and represent energy released to the thermal bath. Hence, the influence of the electric field on the spin–lattice relaxation is small and the $T_1$ times are therefore less affected by the applied HV field.

On the contrary, the temperatures calculated from the $T_2$ times are significantly higher than the temperatures expected from the $T_1$ times. Thus, a smaller response of the spin–lattice relaxation time $T_2$ on temperature is seen when an HV is applied to glycerol.

The authors conclude that these observations point toward a population of molecules in a glycerol EHD bridge where
protons are more mobile in the electrically stressed liquid compared to the glycerol in the bulk not affected by voltage. These results also support the hypothesis that, similar to water, this higher proton mobility and stronger delocalization might have an effect on the physical properties of electrically stressed glycerol, e.g., viscosity. Under the influence of HV, a change in physical properties in glycerol occurs, an effect similar to the one observed in electrically stressed water.7

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**Notes**
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