Dielectric spectroscopy on aqueous electrolytic solutions

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Abstract In this work, detailed dielectric measurements are presented on aqueous electrolytic solutions of NaCl and KCl in a broad frequency range, typical for modern telecommunication techniques. The complex dielectric permittivity or equivalently the complex conductivity are systematically studied as function of frequency (100 MHz– 40 GHz), temperature $(10-60^{\circ}\text{C})$ and molar concentration (0.001–1 mol/l). By a detailed analysis of the dielectric results using an asymmetrically broadened Cole–Davidson distribution of relaxation times, in addition to dc conductivity, the dielectric response as function of frequency, temperature, and molar concentration was fully parameterized by a total of 13 parameters. This model ansatz and the 13 parameters include an enormous predictive power, allowing a reasonable estimation of the dielectric constant, loss, and the conductivity for any set of external variables frequency, temperature and concentration. The proposed method is not only useful for rather simple electrolytic solutions, but also for cell suspensions and biological matter, if additional processes, especially at low frequencies, are adequately taken into account.

Introduction

Dissolved salts have a significant effect on the dielectric properties of water: their ionic conduction drastically increases the dc conductivity, and aqueous solutions are generally assumed to be good ion conductors, due to the

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unique dielectric and viscous properties of water. In addition, the static dielectric constant and the relaxation dynamics of the water molecules are significantly altered. Nowadays this is standard knowledge and extensively discussed in textbooks (see, e.g., [\[1](#page-6-0)]) and recent literature (e.g., [\[2–6](#page-6-0)]). There, the concentration dependences of the static dielectric constants [[1,](#page-6-0) [3,](#page-6-0) [4\]](#page-6-0) or of the mean relaxation times [[3,](#page-6-0) [4](#page-6-0)] for different ion species are plotted or tabulated at a given temperature [[1,](#page-6-0) [3,](#page-6-0) [4\]](#page-6-0). The dielectric properties of electrolytes have an enormous impact on a variety of physical and chemical properties and are also of considerable technical relevance [[3,](#page-6-0) [4\]](#page-6-0). In recent years, renewed interest arose because of their importance for the absorption of electromagnetic radiation by biological matter [\[7](#page-6-0)]. The so-called ''Specific Absorption Rate'' (SAR) employed to quantify the absorption of electromagnetic radiation by living organisms is mainly determined through the conductivity of electrolytes. Via the reflection coefficient, the real part of the dielectric permittivity (the ''dielectric constant", ε') determines the absorption of radiation by the body, and via its influence on the wavelength, ε' is also of relevance for possible resonance effects within the body. Hence, precise knowledge of the dielectric properties of electrolytes as function of frequency, temperature and concentration of the ionic solution, is extremely important. However, it is rather cumbersome to predict the absorption of electromagnetic radiation on the basis of tables and figures taken from the literature. In the present paper it is documented that it is possible to provide a set of 13 parameters which uniquely describe the frequency, temperature and concentration dependence for aqueous solutions of a given ionic species. A similar task was already undertaken in [[8](#page-6-0), [9](#page-6-0)]. However, in the present work more materials are investigated and a broader frequency and temperature range is covered. In addition, it is proposed here to trace back the observed behavior to a smaller number of more basic parameters such as the energy barriers of Arrhenius laws. The present work is intended to provide an example for the feasibility of this method. Especially in the technically relevant frequency range investigated in the present work, the response of most biological materials is qualitatively similar to that of the investigated simple electrolytes. Thus, this method can also be used for the prediction of properties of more complex biological systems. If additional processes at low frequencies can adequately taken into account, this will ultimately allow determination of SAR values for any given frequency or temperature.

In the present work, detailed dielectric investigations of aqueous solutions of NaCl and KCl are presented, for frequencies between 100 MHz and 40 GHz, temperatures from 10 to 60° C, and molar concentrations between 0.001 and 1 mol/l. In general, the precision of the results at least matches or surpasses the most previously published data. The dielectric data are parameterized utilizing the sum of a Cole–Davidson function and a dc conductivity contribution. It is demonstrated that a total of 13 parameters allows calculation of the complex dielectric permittivity for any combination of values of frequency, temperature and concentration.

Materials and methods

The complex dielectric permittivities of aqueous solutions were determined for frequencies between 100 MHz and 40 GHz, by means of an open-end coaxial line method using an Agilent E8363B PNA Network Analyzer and a socalled ''slim-form'' probe from an Agilent 85070E Dielectric Probe Kit. In this method, the reflection of a coaxial line, whose end is immersed into the sample material, is measured. The dielectric properties are calculated taking into account the electric field distribution at the end of the line [[10,](#page-6-0) [11\]](#page-6-0). Eppendorf Micro Test Tubes (1.5 ml) were used and put into an Eppendorf thermomixer to ensure a constant and stable temperature profile for the solutions, and high homogeneity of the concentration of the electrolyte. The temperature was determined and stabilized better than 0.1°C. The measurements were performed at 17 temperatures between 10 and 60° C, i.e., 10, 20, 24–50 $^{\circ}$ C in steps of 2, and 60°C, respectively. The electrolytic solutions (KCl and NaCl) were purchased from Merck ("Certipure® grade") and Sigma-Aldrich ("Standard solution", salt concentration $\pm 0.1\%$, Salt > 99% purity), respectively. All concentrations in this work are expressed in molarity (mol/l), determined at room temperature. Overall, four different KCl solutions (0.001, 0.01, 0.1 and

1 mol/l) and five different NaCl solutions (0.01, 0.1, 0.154, 0.5 and 1 mol/l) were investigated.

Data analysis

The measured frequency-dependent dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was fitted utilizing the sum of a relaxation function and a contribution from pure dc conductivity σ_{dc} . While the latter accounts for the ionic charge transport, the relaxation function describes the loss peak and step-like decrease in ε' that are also observed in pure water. Before systematically analyzing the dielectric spectra, the most commonly employed relaxation functions were tested, namely the Debye function, the symmetrically broadened Cole–Cole function [\[12](#page-7-0)], and the asymmetrically broadened Cole–Davidson (CD) function [[13\]](#page-7-0). At room temperature, the relaxation peak is located close to a frequency of 20 GHz and it shifts to lower/higher frequencies when the temperature decreases/increases. Thus, to check for the best suited relaxation function, only results at low temperatures were considered, where the measured frequency range also covers the high-frequency flank of the relaxation peak. These tests revealed that a mono-dispersive Debye relaxation does not provide a satisfactory fit of the data and that a CD function, corresponding to an asymmetrically broadened distribution of the relaxation time, yields slightly better results than a symmetrically broadened Cole–Cole function. For other polar liquids, the CD function was also found to provide satisfactory fits (see, e.g., $[14-16]$). Thus, the frequency-dependent complex permittivity was fitted using the following formula:

$$
\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{\rm s} - \varepsilon_{\infty}}{\left[1 + (i\omega\tau)\right]^{\beta}} - i\frac{\sigma_{\rm dc}}{\varepsilon_0\omega} \tag{1}
$$

where ε_{∞} is the high-frequency dielectric constant, $\varepsilon_{\rm s}$ is the static (low-frequency) dielectric constant, τ the relaxation time, β the asymmetry parameter which is 1 in the Debye case, σ_{dc} is the dc conductivity, and ε_0 the dielectric permittivity of vacuum.

Using Eq. 1, the least-square fits were simultaneously performed for the real and imaginary parts.

For the temperature dependence of mean relaxation time τ and dc conductivity, one can assume a thermally activated (Arrhenius) behavior (Eqs. 2 and 3):

$$
\tau = \tau_0 \exp\left(\frac{E_\tau}{k_B T}\right) \tag{2}
$$

$$
\sigma_{\rm dc} = \sigma_0 \exp\left(-\frac{E_\sigma}{k_{\rm B}T}\right) \tag{3}
$$

where E_{τ} and E_{σ} can be assumed to be hindering barriers against thermal reorientation of the water molecules and against thermally activated diffusion of the dissolved ions, and τ_0 and σ_0 are factors.

For ionic conduction, the latter (σ_0) should exhibit an inverse linear temperature dependence. This has been neglected here as, due to the relatively narrow temperature interval of the present experiments, this linear temperature dependence was considered negligible when compared to the exponential function describing the Arrhenius behavior. For the dielectric strength $(\Delta \varepsilon = \varepsilon_{\rm s} - \varepsilon_{\infty})$ of dipolar materials, based on the Onsager theory a Curie law $(\Delta \varepsilon \sim 1/T)$, can be expected; however, in the present case it can be better parameterized utilizing the phenomenological Curie–Weiss law (Eq. 4):

$$
\Delta \varepsilon = \frac{C}{T - \theta} \tag{4}
$$

A stronger temperature dependence of $\Delta \varepsilon$ than implied in the Curie behavior is a phenomenon often observed in polar liquids pointing to cooperative relaxation processes [\[14](#page-7-0), [15\]](#page-7-0). The Curie–Weiss law signifies dipole–dipole interactions with $k_B\theta$ characterizing the interaction strength. The constant C is related to the apparent dipole moment of the water molecules in the electrolyte.

Of course, most of the constants τ_0 , E_{τ} , σ_0 , E_{σ} , C and θ , which characterize the complete temperature dependence of the dielectric response of the investigated solutions, should significantly depend on ion concentration. For simplicity reasons, the concentration dependences of all these parameters P were parameterized by a linear behavior (Eq. 5):

$$
P = A(P) + B(P)c \tag{5}
$$

where c is the molar concentration in mol/l.

Only for σ_0 the constant $A(\sigma_0)$ becomes zero as it is evident that for $c = 0$ the conductivity should vanish (neglecting impurities and the small intrinsic conductivity of pure water). Equation 5 should be taken as a first approximation only, and it may not be strictly valid at low and high concentrations. More measurements at other concentrations are necessary to find a more precise parameterization, for example, by introducing higher-order polynomials. Overall 11 parameters were introduced to describe the concentration dependence of the constants τ_0 , E_{τ} , σ_0 , E_{σ} , C and θ in addition to the static dielectric constant ε_s , the high-frequency value ε_{∞} (both being correlated via $\Delta \varepsilon = \varepsilon_{\rm s} - \varepsilon_{\infty}$), and the asymmetry parameter β . Due to the restricted frequency range at the high-frequency flank of the dielectric loss peak, the latter is difficult to determine from our experiments. Therefore, a constant value of β for all concentrations was assumed as detailed in the next section. Note that the parameter ε_{∞} can hardly be determined from our experiments and, therefore, a constant value was taken from the literature [[1,](#page-6-0) [7](#page-6-0)] and fixed in the fits to $\varepsilon_{\infty} = 4$. A possible weak concentration dependence is not expected to influence the fit results in the frequency range investigated in this work. With this approach, ε _s is completely determined by the Curie–Weiss parameters for $\Delta \varepsilon$. Thus, overall we have a set of 13 parameters. In the following section it is shown that these parameters, when experimentally determined, uniquely describe the complex dielectric permittivity or equivalently the complex conductivity $(\sigma^* = \sigma' + i\sigma' = i\varepsilon^* \varepsilon_0 \omega)$ for any given values of frequency, temperature and concentration.

Results and discussion

Figure [1](#page-3-0) shows the dielectric constant (a), the dielectric loss (b) and the real part of the conductivity (c) as function of frequency for a 0.01 molarity KCl solution at temperatures between 10 and 60° C. The real part of the dielectric constant reveals a low-frequency plateau corresponding to ε _s, which significantly decreases with increasing temperature. Toward high frequencies a step-like decrease shows up, indicative for the characteristic relaxational process of the water molecules. Correspondingly, $\varepsilon''(v)$ shows the typical loss peaks. The peak maximum, which is well defined except for the highest temperatures, significantly shifts to lower frequencies with decreasing temperature, indicating an increase of the mean relaxation time due to slowing down of the re-orientational motions of the water molecules. The strong increase in $\varepsilon''(v)$ observed at low frequencies can be ascribed to ionic charge transport. In the double-logarithmic plot of Fig. [1b](#page-3-0), it has a slope of -1 and thus $\varepsilon'' \sim v^{-1}$. As $\sigma' = \varepsilon_0 \varepsilon'' \omega$, this low-frequency divergence of the loss corresponds to a constant σ' , i.e., dc conductivity. As revealed by Fig. [1](#page-3-0)c, which shows the frequency and temperature dependence of the real part of the conductivity, indeed a frequency-independent low-frequency plateau is present, indicating pure dc conductivity. The plateau value increases approximately by a factor of 2 when the temperature is raised from 10 to 60° C. The solid lines in Fig. [1](#page-3-0) correspond to fits as outlined in the previous section, utilizing a CD function and a dc conductivity contribution (Eq. [1\)](#page-1-0). At the lowest frequencies and high temperatures, $\varepsilon'(v)$ is no longer constant and the slope of $\varepsilon''(v)$ deviates from a v^{-1} -behavior. These deviations scale well with the dc conductivity, becoming stronger for higher σ_{dc} . Such behavior can be ascribed to the onset of blockingelectrode-effects [\[17](#page-7-0)]. Blocking electrodes usually come into play at low frequencies and/or high ionic conductivity when thin layers of counter ions at the electrodes hamper further diffusion of ions in the electrolyte. As for the rel-atively low ion concentrations of Fig. [1](#page-3-0) ($c = 0.01$ mol/l), these effects are rather weak, they can be assumed to have

Fig. 1 a Dielectric constant, b dielectric loss and c real part of the conductivity, as a function of frequency for a 0.01 mol/l KCl solution measured at temperatures between 10 and 60°C. The solid lines are fits using Eq. [1](#page-1-0). The *dashed line* was calculated for 30° C, based on the parameters of Table [1](#page-5-0)

only small influence on the properties at higher frequencies, and the fits have been restricted to the region beyond the range where blocking electrodes may become important. Nevertheless, measurements at lower frequencies than those used here would be desirable, to enable a correct modeling of the electrode effects and to get a more precise estimate of the absolute values of the fit parameters in Eq. [1.](#page-1-0)

Figure 2 shows similar results on NaCl electrolytes. In this figure, the real (a) and imaginary (b) parts of the dielectric permittivity is plotted, as is the conductivity (c) measured as a function of frequency at a temperature of 37°C, for molar concentrations ranging from 0.01 to 1 mol/l. At higher molar concentrations the peak of the water relaxation in ε'' is almost hidden by conductivity contributions. Again the solid lines in Fig. 2 correspond to the results of fits using Eq. [1.](#page-1-0) At high molar concentrations, the dielectric constant reveals a strong increase of $\varepsilon'(v)$ toward low frequencies, which can be ascribed to pronounced electrode polarization effects. To corroborate this interpretation, for $c = 1$ mol/l, two room temperature measurements were performed with the ''slim-form'' coaxial probe and a coaxial line with larger diameter (Agilent ''High Temperature Probe''). As expected for blocking electrodes, a shift of the ε' -increase to lower frequencies was found for the larger diameter probe. In the fits shown in Fig. 2, the electrode effects were taken into

Fig. 2 a Dielectric constant, b dielectric loss and c real part of the conductivity, as function of frequency for NaCl solutions with ion concentrations ranging from 0.01 to 1 mol/l measured at a temperature of 37° C. The solid lines are fits using Eq. [1.](#page-1-0) The dashed lines were calculated for concentrations of $c = 0.01$ and 1 mol/l, based on the parameters of Table [1](#page-5-0)

account using the commonly applied description with a parallel RC circuit in series to the sample [\[17](#page-7-0)]. Fits with and without this contribution (in the latter case restricting the fits to high frequencies) lead to small but significant differences also for the bulk parameters of Eq. [1](#page-1-0) (especially for $\Delta \varepsilon$). This demonstrates the above-mentioned importance of low-frequency measurements for a more precise description also at low ion concentrations.

Similar fits were performed for all data sets obtained for all investigated concentrations of both ion species at temperatures between 10 and 60° C. In a first step, from the results of these fits the temperature dependence of the primary parameters of Eq. [1](#page-1-0) was determined, namely the dc conductivity, the relaxation time and the dielectric strength, respectively. Representative results for NaCl electrolytes with various concentrations are provided in Fig. [3](#page-4-0). Here σ_{dc} (a) and τ (b) are shown in an Arrheniustype representation, while the dielectric strength $\Delta \varepsilon$ (c) is plotted as $1/\Delta \varepsilon$ versus T, to account for the Curie–Weiss type temperature dependence. The solid lines in Fig. [3](#page-4-0) are fit curves indicating a thermally activated behavior of conductivity and relaxation time (Eqs. [2](#page-1-0) and [3,](#page-1-0) respectively) and a Curie–Weiss behavior of the dielectric strength (Eq. [4](#page-2-0)). For low temperatures, a width parameter $\beta \approx 0.95$ was found, only weakly varying with temperature and concentration. For high temperatures it is difficult to obtain a reliable estimate for β as it is mainly based on

Fig. 3 Temperature dependence of the fit parameters as obtained from the description of the dielectric spectra with Eq. [1](#page-1-0) for selected aqueous NaCl solutions. The dc conductivity (a) and relaxation time (b) are shown in an Arrhenius-type representation, while the dielectric strength (c), is plotted as $100/\Delta\varepsilon$ versus T. The lines are linear fits and demonstrate the Arrhenius-like behavior of σ_{dc} and the Curie–Weisslike behavior of $\Delta \varepsilon$

the high-frequency flank of the relaxation peak. Therefore it was fixed to a temperature-independent value of 0.95. Similar fits as shown in Fig. 3 were performed for all investigated concentrations of both ion species. This procedure leads to the relevant concentration-dependent parameters characterizing the temperature dependences of the dielectric response for different ion contents, i.e., the energy barriers governing the reorientation of the water molecules (E_z) , the energy barriers determining the ionic diffusion (E_{σ}) , the pre-factors of the Arrhenius laws for both processes (τ_0 and σ_0), as well as the Curie–Weiss parameters C and θ .

In a second step, the dependences of these parameters on molar concentration were parameterized. The concentration dependences of the energy barriers and the pre-factors for both electrolytes are documented in Fig. 4a–d, while the parameters of the Curie–Weiss law for both sets of data are shown in Fig. 4e, f. As detailed in the preceding section, for simplicity reasons the concentration dependences were fitted by a linear behavior (Eq. [5\)](#page-2-0), and the results of these fits are shown as solid lines in Fig. 4 (because in Fig. 4a semi-logarithmic scale is used, the linear fits appear

Fig. 4 Concentration dependences of pre-factors (a, c), energy barriers (b, d) and Curie–Weiss parameters (e, f) for both electrolytes. The lines are fits using Eq. [5](#page-2-0)

curved). However, one should be aware that this linear description may only be a rough approximation of the actual dependence. For example, it is well known that at high concentrations interactions between the ions can lead to a reduction of the conductivity $[18]$ $[18]$, a behavior that certainly is not covered here. To overcome this problem, more concentrations should be investigated and the uncertainties of the parameters in Fig. 4 should be reduced, to arrive at a more precise description. However, for the purpose of the present work which was intended to demonstrate the principle feasibility of this approach, a linear description may be sufficient. Note that the present approach is different to that described in [[8\]](#page-6-0), where the concentration and temperature dependences of ε_{s} , τ , and σ_{dc} of NaCl solutions were parameterized by rather complex polynomial expressions. In the present work, the temperature dependences were traced back to Eqs. [2](#page-1-0)[–4](#page-2-0) and only the concentration dependences of the involved quantities (e.g., E_{τ} or θ) were parameterized, which leads to a much smaller total number of required parameters.

In Table [1](#page-5-0) the 13 parameters as obtained from the fits of the experimental data are summarized. Together with Eqs. [1–](#page-1-0)[5](#page-2-0) they should allow for a complete description of the complex dielectric permittivity and the complex conductivity as a function of frequency, temperature and concentration. To check for consistency, in Figs. [1](#page-3-0) and [2](#page-3-0) typical curves were included that were calculated on the basis of the values given in Table [1](#page-5-0) (dashed lines), revealing a reasonable agreement with the experimental data. To confirm the predictive power of the formalism developed here, the results calculated with our formalism were also compared with results reported in the literature. Figure [5](#page-5-0)

 $B(C)$ (K l/mol) $-3,930 \pm 1,000$ $-2,450 \pm 1,000$ $A(\theta)$ (K) 119 ± 15 126 ± 15 $B(\theta)$ (K l/mol) 11.5 \pm 20 1.21 \pm 20

Note that the asymmetry parameter β was fitted at low temperatures only and kept fixed for $T > 30$ ^oC

shows the obtained concentration dependences of the dielectric permittivity and of the conductivity at 37°C and 100 MHz for NaCl and KCl electrolytes. For both ion species we find significant concentration dependences, while loss and conductivity reveal an almost linear increase with concentration; the dielectric constant exhibits a plateau at low and a significant decrease at higher concentrations. Figures [1](#page-3-0) and [2](#page-3-0) suggest the ε' at 100 MHz to correspond to ε _s. The solid line in Fig. 5a was calculated from an empirical expression for $\varepsilon_{s}(c)$ that was derived by Hasted [\[1](#page-6-0), [19](#page-7-0)], based on the experimental data. According to [\[1](#page-6-0), [19\]](#page-7-0), NaCl and KCl electrolytes should behave identical, while the present approach predicts small but distinct differences in the conductivity as well as in the dielectric increment. In general, the overall behavior is surprisingly well reproduced by our calculated curves, given the rather crude and oversimplified linear description of the concentration dependences (Fig. [4](#page-4-0)). The same holds if our results are compared with the dashed lines in Fig. 5a, c, which were calculated as suggested by [\[8](#page-6-0)], based on the measurements of NaCl solutions. It is interesting that, for $\varepsilon''(c)$ and $\sigma'(c)$ (Fig. 5b, c) at high concentrations our results predict a small deviation from the linear increase. This may well correspond to the long-known occurrence of a less than linear concentration dependence of the conductivity of solutions of salt in polar liquids [\[20](#page-7-0)], which can be explained, for example, by the Debye–Hückel theory $[21, 22]$ $[21, 22]$ $[21, 22]$ $[21, 22]$. As a further check of our approach, in Fig. [6](#page-6-0) the concentration dependence of the mean relaxation time of NaCl electrolytes at 20°C is shown and compared to literature values. Again, experimental data and calculated curve agree reasonably well. Finally, Fig. [7](#page-6-0) shows the frequency dependence of the permittivity of two NaCl solutions as reported in [\[3](#page-6-0)]. Again the curves calculated according to our approach agree reasonably well with the literature data. The deviations at the low-frequency flank of the loss peak may indicate a small

Fig. 5 Concentration dependences of the dielectric constant (a), loss (b) and conductivity (c) at 100 MHz for NaCl and KCl electrolytes, respectively, calculated using Eqs. [1](#page-1-0)[–5](#page-2-0) with the parameters given in Table 1 (symbols). The solid line in **a** and the *dashed lines* in **a** and **b** were calculated using the empirical relations provided in [[1](#page-6-0), [19](#page-7-0)] and [[8](#page-6-0)], respectively

departure from the linear increase predicted by Eq. [1](#page-1-0); however, one should be aware that in [[3\]](#page-6-0) the dc conductivity was subtracted from the raw data and that the low-frequency slope of loss peaks critically depends on the exact value that was subtracted. It is noted that the absolute values of the dielectric constant calculated from our approach appear to be higher than those from the literature (cf. Figs. 5a, [7](#page-6-0)). At higher concentrations, the present data were fitted including blocking-electrode contributions, and it was

Table 1 calculati

Fig. 6 Concentration dependence of the relaxation time of NaCl electrolytes (τ_s) , related to that of pure water (τ_w) . The line was calculated using Eqs. [2](#page-1-0) and [5](#page-2-0) and the parameters given in Table [1](#page-5-0). The *circles* show literature data taken from [2]

Fig. 7 Frequency dependence of dielectric constant and loss from [3] (symbols) for two NaCl solutions. The lines were calculated using Eqs. [1,](#page-1-0) [2](#page-1-0), [4](#page-2-0) and [5](#page-2-0). The conductivity was set to zero as in $[3]$, where the dc conductivity was subtracted

found that via their capacitance connected in series to the bulk sample, blocking electrodes can lead to a reduction of the low-frequency plateau value of $\varepsilon'(v)$. Then the actual value of the intrinsic static dielectric constant of the relaxation is higher than the value deduced from the plots or obtained from fits that do not take blocking effects into account. This is an interesting fact and worth to be investigated further. Clearly, broadband measurements extending to lower frequencies are necessary to check for the significance of the blocking-electrode effects and to reveal the actual value of the static dielectric constant in aqueous solutions. This could be done, for example, by performing measurements below the GHz range using conventional capacitor geometry and different electrode spacings.

Conclusion

In summary, it is demonstrated in the present paper that a set of 13 parameters, determined from a systematic investigation of the dielectric response of aqueous solutions, allows a reasonable estimate of the dielectric properties for any combination of temperature, frequency and ion concentration. Although the present data were obtained in a restricted temperature and frequency range and analyzed by rather simple formulas, a reasonable prediction of experimental values was already possible. In a next step, it is planned to improve the precision of this approach by performing broadband dielectric spectroscopy employing a combination of state-of-the-art experimental setups as it is used for example in the investigation of super-cooled liquids [[14,](#page-7-0) [15](#page-7-0), [23](#page-7-0), [24\]](#page-7-0). This approach is expected to reduce the considerable uncertainties involved in the determination of most parameters (cf. error bars in Fig. [4](#page-4-0)), and to develop the present approach as a powerful tool for the prediction of the response of electrolyte solutions to electromagnetic fields.

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References

- 1. Hasted JB (1973) Electrolytic solutions. In: Aqueous dielectrics. Chapman & Hall, London, pp 136–174
- 2. Nörtemann K, Hilland J, Kaatze U (1997) Dielectric properties of aqueous NaCl solutions at microwave frequencies. J Phys Chem A 101:6864–6869
- 3. Buchner R, Hefter GT, May PM (1999) Dielectric relaxation of aqueous NaCl solutions. J Phys Chem A 103:1–9
- 4. Chen T, Hefter G, Buchner R (2003) Dielectric spectroscopy of aqueous solutions of KCl and CsCl. J Phys Chem A 107:4025– 4031
- 5. Wachter W, Kunz W, Buchner R, Hefter G (2005) Is there an anionic Hofmeister effect on water dynamics? Dielectric spectroscopy of aqueous solutions of NaBr, NaI, NaNO₃, NaClO₄, and NaSCN. J Phys Chem A 109:8675–8683
- 6. Wachter W, Fernandez S, Buchner R, Hefter G (2007) Ion association and hydration in aqueous solutions of LiCl and Li2SO⁴ by dielectric spectroscopy. J Phys Chem B 111:9010– 9017
- 7. Loidl A, Lunkenheimer P, Gulich R, Wixforth A, Schneider M, Hänggi P, Schmid G (2006) Untersuchungen zu der Fragestellung, ob makroskopische dielektrische Gewebeeigenschaften auch auf Zellebene bzw. im subzellulären Bereich uneingeschränkte Gültigkeit besitzen: Bestandsaufnahme. [http://www.emf-forschungsprogramm.de/forschung/dosimetrie/](http://www.emf-forschungsprogramm.de/forschung/dosimetrie/dosimetrie_verg/dosi_075_ZwB_01.pdf) [dosimetrie_verg/dosi_075_ZwB_01.pdf.](http://www.emf-forschungsprogramm.de/forschung/dosimetrie/dosimetrie_verg/dosi_075_ZwB_01.pdf) Cited 3 Apr 2008
- 8. Peyman A, Gabriel C, Grant EH (2007) Complex permittivity of sodium chloride solutions at microwave frequencies. Bioelectromagnetics 28:264–274
- 9. Stogryn A (1971) Equations for calculating the dielectric constant of saline water. IEEE Trans Microwave Theory Tech MT19:733
- 10. Wei Y-Z, Sridhar S (1989) Technique for measuring the frequency-dependent complex dielectric-constants of liquids up to 20 GHz. Rev Sci Instrum 60:3041–3046
- 11. Jiang GQ, Wong WH, Raskovich EY, Clark WG, Hines WA, Sanny J (1993) Open-ended coaxial-line technique for the measurement of the microwave dielectric-constant for low-loss solids and liquids. Rev Sci Instrum 64:1614–1621
- 12. Cole KS, Cole RH (1941) Dispersion and absorption in dielectrics. J Chem Phys 9:341–351
- 13. Davidson DW, Cole RH (1950) Dielectric relaxation in glycerine. J Chem Phys 18:1417
- 14. Lunkenheimer P, Schneider U, Brand R, Loidl A (2000) Glassy dynamics. Contemp Phys 41:15–36
- 15. Lunkenheimer P, Loidl A (2002) Dielectric spectroscopy of glass-forming materials: a-relaxation and excess wing. Chem Phys 284:205–219
- 16. Brand R, Lunkenheimer P, Schneider U, Loidl A (2000) Excess wing in the dielectric loss of glass-forming ethanol: a relaxation process. Phys Rev B 62:8878–8883
- 17. Macdonald JR (1987) Impedance spectroscopy. Wiley, New York
- 18. Howell FS, Moynihan CT, Macedo PB (1984) Electrical relaxations in mixtures of lithium-chloride and glycerol. Bull Chem Soc Jpn 57:652–661
- 19. Hasted JB, Ritson DM, Collie CH (1948) Dielectric properties of aqueous ionic solutions. Parts I and II. J Chem Phys 16:1–21
- 20. Kohlrausch F, Holborn L (1916) Das Leitvermögen der Elektrolyte. Teubner, Leipzig
- 21. Debye P, Hückel E (1923) Zur Theorie der Elektrolyte.I.Gefrierpunktserniedrigungen und verwandte Erscheinungen. Phys Zeitschrift 24:185–206
- 22. Debye P, Hückel E (1923) Zur Theorie der Elektrolyte.II.Das Grenzgesetz für die elektrische Leitfähigkeit. Phys Zeitschrift 24:305–325
- 23. Schneider U, Lunkenheimer P, Pimenov A, Brand R, Loidl A (2001) Wide range dielectric spectroscopy on glass-forming materials: an experimental overview. Ferroelectrics 249:89–98
- 24. Lunkenheimer P, Loidl A (2003) Response of disordered matter to electromagnetic fields. Phys Rev Lett 91:207601-1-207601-4