Dielectric Properties of Aqueous NaCl Solutions at Microwave Frequencies

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At 20 °C the complex (electric) permittivity of aqueous solutions of sodium chloride has been measured as a function of frequency ν (20 MHz $\leq \nu \leq$ 40 GHz) and salt content ($0.003 \leq y \leq 0.035$; y, mass fraction of NaCl). The dielectric part of the spectra has been represented by the semiempirical Cole−Cole relaxation spectral function to yield the extrapolated low-frequency (static) permittivity $\epsilon(0)$ and the principal relaxation time τ_s of the solutions. At $c > 0.2$ mol/L the extrapolated permittivity follows the linear relation $\epsilon(0) = \epsilon_w(0)\,(1 - 0.19\ (\text{mol/L})^{-1}\,c)$ where $\epsilon_w(0)$ denotes the static permittivity of water at 20 °C. This dielectric decrement is related to the effects of dilution of the dipolar solvent, of kinetic depolarization, and of structure saturation. At lower NaCl concentration ($c < 0.2$ mol/L) small indications for an additional polarization mechanism are found. The principal dielectric relaxation time linearly decreases with the solute molality m. The relative molal shift in τ_s appears to be stronger at 20 °C ($-(0.15 \pm 0.06)\ (\text{mol/kg})^{-1}$) than at higher temperatures ($-(0.08 \pm 0.03)\ (\text{mol/kg})^{-1}$, 25 °C). Mechanisms that might lead to a reduction of the relaxation time on addition of salt are briefly presented.

1. Introduction

The dielectric properties of aqeuous electrolyte solutions are of considerable importance for our understanding of the hydration[1,2] and complexation[3,4] behavior of ions, particularly for our knowledge of related elementary mechanisms in liquids, such as electric conductivity,[2,5] structure saturation,[6,7] dielectric friction,[8,9] and kinetic depolarization.[9−11] Besides such fundamental aspects, interest in electromagnetic wave interactions with saline solutions also springs from a variety of applications, including the use of microwaves as sensors in the measurements of the water content in soils[12,13] and in the noninvasive moisture determination of many materials.[13,14] Due to the current lively electromagnetic compatibility debate,[15−17] much attention is also paid to the dielectric properties of cells and biological tissues[18−20] in which accumulation of electrical charges at internal interfaces may lead to special "giant" electric polarization contributions and relaxation phenomena.[21]

Contrary to the major role that aqueous solutions of salts do play in nature, science, and chemical engineering, their dielectric properties are still insufficiently known.[22] One reason for the lack of comprehensive sets of relevant data is the high (specific) electric direct current (dc) conductivity σ which adversely affects measurements of the complex (electric) permittivity

$$\epsilon(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) \tag{1}$$

of electrolyte solutions as a function of frequency ν. The (negative) imaginary part of the permittivity of conducting samples contains two contributions

$$\epsilon''(\nu) = \epsilon''_d(\nu) + \epsilon''_\sigma(\nu) \tag{2}$$

of which ϵ''_d represents the dielectric loss and ϵ''_σ the loss due to the drift of ions. Since the latter is given by the relation

$$\epsilon''_\sigma(\nu) = \sigma/(\epsilon_0\omega) \tag{3}$$

it tends to mask the dielectric contribution at low frequencies. In eq 3 ϵ_0 denotes the electric field constant, and $\omega = 2\pi\nu$ is the angular frequency. Besides this masking effect, a high conductivity impedes dielectric measurements by imposing a small resistance on any suitable specimen cell and also by potential space charge polarization effects at the liquid/electrode interface.[23] Consequently, even appropriate dielectric reference data of strongly conducting solutions are just scarcely available.

In this situation we found it useful to measure the complex permittivity of aqueous NaCl solutions as a function of frequency (20 MHz $\leq \nu \leq$ 40 GHz) and salt content (up to 3.5% w/w). In order to ensure the absence of systematic errors, measurements have been performed applying four different methods. The resulting spectra are analyzed in terms of a semiempirical relaxation function, the parameters of which are discussed to examine attributes of the liquid structure and the microdynamics of saline solutions.

2. Experimental Section

Complex Permittivity Measurements. In order to reduce effects of potential systematic errors, four different methods of measurement have been applied to cover the frequency range from 20 MHz to 40 GHz, and altogether 10 different specimen cells have been used. The cells were made of silver, stainless steel, or were covered with a layer of gold or platinum (Drittes Physikalisches Institut, DPI) or with a Sucoplate alloy consisting of zinc, copper, and tin (Christian Michelsen Research, CMR). At the DPI three well-tried methods were available. At CMR a more recently developed technique was utilized.

Between 0.02 and 2 GHz at the DPI the complex permittivity has been derived from the complex reflection coefficient of a cut-off type specimen cell.[26] The cell was connected to a broad band reflection test set (HP 85044A) that in turn was operated by an automatic network analyzer (HP 8753A, 300 kHz $\leq \nu \leq$ 3 GHz). The analyzer was controlled by a laboratory computer that also enabled direct evaluation of the reflected signal. We used a coaxial line/circular waveguide section as specimen cell

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TABLE 1: Experimental Errors in the Complex Permittivity Values Measured at the DPI

ν, GHz	$\Delta\epsilon'/\epsilon'$, %	$\Delta\epsilon''/\epsilon''$, %	ν, GHz	$\Delta\epsilon'/\epsilon'$, %	$\Delta\epsilon''/\epsilon''$, %
0.02−1	1	1	5−18	1	1
1−2	2	1	18−30	2	1
2−5	1	0.7	30−40	4	2

in which the liquid was completely contained in the waveguide ($l = 0$).[26] Due to the high permittivity of the samples, it was sufficient to represent the cells by a simple equivalent network consisting of two capacitances.[26] The values of these capacitances have been found by calibration procedures in which the cell was filled with air or with bidistilled and additionally deionized water as reference.[27]

Above 2 GHz two propagating wave transmission methods have been employed at DPI. Both methods involve a microwave double-beam interferometer technique and enable absolute $\epsilon(\nu)$ measurements. Seven interferometer setups, each matched to a particular frequency range, have been used. One was constructed with coaxial line components ($\nu < 5$ GHz), the others were made of waveguide devices. In one method ($5.3 \leq \nu \leq 8.4$ GHz; $12.4 \leq \nu \leq 18$ GHz), the electromagnetic field within the liquid-filled cell was automatically probed, operating the interferometer in an off-balance mode.[25] For this purpose an antenna immersed in the liquid was precisely shifted along the direction of wave propagation. In the other method ($5.3 \leq \nu \leq 40$ GHz), the cell branch and the reference branch of the interferometer have been carefully adjusted by hand to yield zero output signal of the interferometer assembly.[24]

At CMR an open-ended coaxial probe,[28] similar to devices described previously,[28−33] has been employed. This probe, originally constructed for on-line implementation in process-control circuits, has been provided with a sample container suitable for laboratory use. The specimen cell was connected to a computer-controlled network analyzer (HP 8722C, 50 MHz $\leq \nu \leq$ 40 GHz) to determine the complex reflection coefficient at the liquid/probe interface. The probe properties have been obtained from calibration measurements at 20 °C using air, distilled water,[27] and methanol[34] as reference fluids. In these procedures the methanol (>99%; Merck, Darmstadt, FRG) has been carefully handled in order to avoid water uptake from the air. In principle, the open-ended coaxial probe allows for measurements at frequencies down to below 0.1 GHz. In the present configuration, however, the precision in the data may be reduced at frequencies below 0.5 GHz.[33] For this reason $\epsilon(\nu)$ values from the open-ended probe measurements will be considered in the analytical treatment of spectra between 0.5 and 40 GHz only.

TABLE 2: Mass Fraction y of NaCl, Density ρ of Solution, Solute (c) and Solvent (c_w) Concentration, as Well as Extrapolated Low-Frequency Permittivity $\epsilon(0)$ and Principle Dielectric Relaxation Time τ_s for Aqueous Solutions of Sodium Chloride at 20 °C

y, $\times 10^{-2}$ ±0.1%	ρ, g/mL ±0.1%	c, mol/L ±0.2%	c_w, mol/L ±0.2%	$\epsilon(0)$	τ_s, ps
0	0.9982[37]	0	55.39	80.2 ± 0.2[27,a]	9.36 ± 0.05[27]
0.3	1.0005	0.051	55.3	80.4 ± 0.5	9.28 ± 0.2
1	1.005	0.172	55.1	78.7 ± 0.6	9.0 ± 0.2
1.3	1.0075	0.224	55.1	77.7 ± 0.6	9.0 ± 0.2
2	1.012	0.346	54.9	74.6 ± 0.6	8.9 ± 0.2
2.4	1.015	0.416	54.8	74.9 ± 0.6	8.9 ± 0.2
3	1.0195	0.523	54.8	73.4 ± 0.7	8.7 ± 0.2
3.5	1.023	0.612	54.7	72.0 ± 0.6	8.7 ± 0.2

[a] Within the limits of error this value extrapolated from the microwave dielectric spectrum agrees with the static permittivity as measured by several authors at low frequencies.[38]

Experimental Errors. All specimen cells were surrounded by a coat for circulating thermostat fluid. At the DPI the temperature T was measured and kept constant to within ±0.05 K. At CMR the fluctuations in T were smaller than 0.1 K. The error in the frequency ν of measurement was smaller than 0.1% throughout. The experimental errors in the reflection coefficient method used below 2 GHz have been derived from repeated measurements in which different cells or different reference liquids have been included. At the low-frequency wing of the spectra ($\nu < 0.06$ GHz), data that were obviously affected by electrode polarization effects have been omitted from the evaluation procedure. Estimates of possible errors in the wave transmission method have been obtained from multiple measurements using different cells and different microwave devices. Attention has been particularly given to the fit of spot frequency data to one another. As discussed in detail previously[4] the experimental error depends significantly on the conductivity σ of the samples. A global characterization of the accuracy of the measurements at the DPI is given in Table 1. The uncertainty in the CMR data has been estimated to be smaller than ±2 in both ϵ' and ϵ'' at $\nu < 1$ GHz and smaller than ±1 at $\nu > 1$ GHz.

Aqueous Solutions. Seven solutions with salinities up to 3.5% by weight have been prepared by weighing appropriate amounts of sodium chloride (>99.8%) and distilled water. The highest NaCl concentration considered in this study corresponds to the salinity of sea water.[34] The NaCl content of another sample (1% w/w) is close to that of the physiological salt solution (0.95% w/w).

The density ρ of the samples has been measured with the aid of a pycnometer that had been calibrated against degassed, deionized, and distilled water. The ρ values as well as the solute (c) and solvent (c_w) concentrations are represented in Table 2. The specific electric conductivity σ has been determined using a two-electrode capillary cell[4] as proposed previously.[36] To apply for strongly conducting liquids, this cell was provided with a high cell constant (48 680 m^{-1}). In order to reduce errors by electrode polarization effects, the ring-shaped electrodes of the cell had been covered by a deposit of finely divided black platinum. The cell resistance has been measured in the usual manner at frequencies between 100 Hz and 100 kHz by comparison with the resistance of a precise decade resistor. The cell was directly immersed in the bath of a thermostat, filled with silicone oil. The sample temperature was stabilized to within ±0.05 K during the conductivity measurements.

3. Results and Treatment of Data

Within the frequency range under consideration the complex dielectric spectrum of water (w) can be represented by a Debye-type relaxation function[39] $R_D(\nu)$ with discrete relaxation time τ_w

$$R_D(\nu) = \epsilon_w(\nu) = \epsilon_w(\infty) + \frac{\epsilon_w(0) - \epsilon_w(\infty)}{1 + i\omega\tau_w} \tag{4}$$

with $\epsilon_w(0) = 80.2 \pm 0.2$, $\epsilon_w(\infty) = 5.6 \pm 0.2$, and $\tau_w = (9.36 \pm 0.05)$ ps at 20 °C.[27] The dielectric part $\epsilon_d(\nu) = \epsilon'(\nu) - i\epsilon''_d(\nu)$ of the permittivity spectrum of the NaCl solutions, an example of which is presented in Figure 1, shows indications of a small relaxation time distribution. For this reason, a sum of a Cole−Cole spectral function[40] $R_{CC}(\nu)$ and a conductivity term

$$\begin{aligned} R_m(\nu) = \epsilon(\nu) &= R_{CC}(\nu) - i\epsilon''_\sigma(\nu) \\ &= \epsilon(\infty) + \frac{\epsilon(0) - \epsilon(\infty)}{1 + (i\omega\tau_s)^{1-h}} - i\sigma/(\epsilon_0\omega) \end{aligned} \tag{5}$$

has been used to analytically represent the measured $\epsilon(\nu)$ spectra.

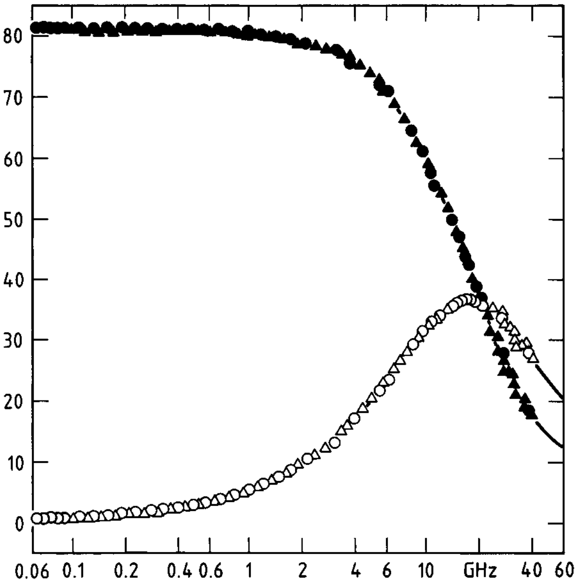

Figure 1. Real part ϵ' (closed symbols) and negative imaginary part ϵ'' (open symbols) of the complex permittivity spectrum of the 0.051 M aqueous solution of NaCl at 20 °C ($y = 0.003$). Points and circles denote data measured at DPI, triangles indicate data from CMR. The curve is the graph of the Cole–Cole function (eq 5).

In eq 5, τ_s denotes the principal relaxation time, and the parameter h measures the width of the underlying (symmetrical) relaxation time distribution. The semiempirical Cole–Cole relaxation function may be questioned for theoretical reasons.[41] It was found, however, that the width of the relaxation time distribution is small throughout ($h = 0.04 \pm 0.02$), in conformity with previous findings for a solution at 25 °C.[42] Hence the Cole–Cole term in the model relaxation spectral function $R_m(\nu)$ nearly equals a Debye term. The $\epsilon(\infty)$ values which are less exactly defined by the measured spectra (Figure 1) have been fixed at $\epsilon_w(\infty) - 1 \leq \epsilon(\infty) \leq \epsilon_w(\infty) + 1$ during the fitting procedures. We thus cannot comment on the correct high-frequency behavior[41] of the solutions. The values of the extrapolated static permittivity $\epsilon(0)$ and of τ_s as found by fitting eq 5 to the measured spectra are compiled in Table 2. A nonlinear least-squares regression analysis, causing the variance

$$\chi^2 = \frac{1}{N - P - 1}\sum_{n=1}^{N} w(\nu_n)|\epsilon(\nu_n) - R_m(\nu_n; \xi_1,...,\xi_P)|^2 \quad (6)$$

to adopt its minimum, has been applied. Here, ν_n ($n = 1, ..., N$) denotes the frequencies of measurement and ξ_p ($p = 1, ..., P$) the unknown parameters of the model function. The $w(\nu_n)$ are weighing factors that are inversely proportional to the experimental errors $\Delta\epsilon'(\nu_n)$, $\Delta\epsilon''(\nu_n)$. The uncertainties given for the parameter values in Table 2 include results from runs in which the relative weights of the data from the two different laboratories have been varied.

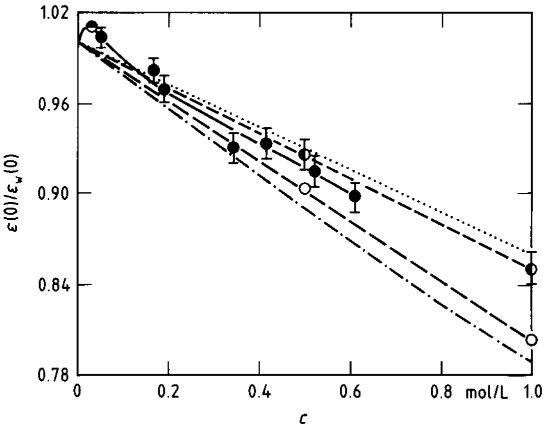

Figure 2. Ratio $\epsilon(0)/\epsilon_w(0)$ of extrapolated static permittivities as a function of solute concentration for NaCl solutions at 20 °C (●, this work; ○, ref 22) and 25 °C (◓, ref 43; ◐, refs 42 and 44). The dotted line represents the $\epsilon(0)/\epsilon_w(0)$-vs-$c$ relation according to Hasted;[6] the dashed-dotted curve, that by Stogryn.[45]

4. Discussion

In Figure 2 the static permittivity ratio $\epsilon(0)/\epsilon_w(0)$ of aqueous NaCl solutions is plotted versus solute concentration c. Also given in that diagram are additional data at 20 °C[22] and at 25 °C[42–44] as well as the graphs of the empirical relations

$$\epsilon(0)/\epsilon_w(0) = 1 - 0.14(\text{mol/L})^{-1}\, c \quad (7)$$

and

$$\epsilon(0)/\epsilon_w(0) = 1 - 0.255(\text{mol/L})^{-1}c + 5.15 \times 10^{-2}(\text{mol/L})^{-2}c^2 - 6.89 \times 10^{-3}(\text{mol/L})^{-3}c^3 \quad (8)$$

given in the literature.[6,45] In conformity with the findings of a very careful study by van Beek of the electric permittivity of conducting solutions at frequencies between 1 MHz and 100 MHz,[43] the extrapolated permittivity at small solute content seems to exceed the static permittivity of water by a small amount ($\epsilon(0)/\epsilon_w(0) = 1.002 \pm 0.007$ at $c = 0.051$ mol/L). A permittivity increment has been assumed[10,43] to result from an ion atmosphere polarization.[5] However, Winsor and Cole[46] have pointed out that, after subtraction of increments according to a speculative extension of the Debye–Falkenhagen theory[5] of dilute electrolyte solutions, a rather unrealistic slope −42 (mol/L)$^{-1}$ in the $\epsilon(0)$-vs-c relation follows from van Beek's data.[10,43] Evidence from our data is too small to comment on the existence of ion atmosphere polarization effects.

At concentrations above 0.2 mol/L a linear relation

$$\epsilon(0)/\epsilon_w(0) = 1 + \delta c \quad (9)$$

follows with $\delta = -0.17$ (mol/L)$^{-1}$. This value appears to constitute a mean of the data by Zasetskii et al.[22] ($\delta = -0.19$ (mol/L)$^{-1}$) and of previous results at 25 °C[42,44] ($\delta = -0.15$ (mol/L)$^{-1}$) as well as of the slopes given by Stogryn[45] (−0.21 (mol/L)$^{-1}$ at $c \to 0$) and by Hasted[6] ($\delta = -0.14$ (mol/L)$^{-1}$, $(\epsilon(0) - \epsilon_w(0))/c = -11$ (mol/L)$^{-1}$).

The decrement in the extrapolated static permittivity of aqueous electrolyte solutions is normally assumed to be due to three effects, (i) dilution of the dipolar solvent and the action of the resulting internal depolarizing fields,[47,48] (ii) kinetic depolarization,[10,11,49–51] and (iii) structure saturation.[52,53] The effects of dilution and internal depolarizing fields may be considered by theoretical mixture relations of which the Bruggeman formula[54]

$$\frac{\epsilon_B - \epsilon_e}{\epsilon_w(0) - \epsilon_e}\left(\frac{\epsilon_w(0)}{\epsilon_B}\right)^{1/3} = 1 - v \quad (10)$$

is displayed in Figure 3. In eq 10 v denotes the volume fraction of solute, ϵ_B is the resulting permittivity of the mixture corresponding with the experimental $\epsilon(0)$ data, and $\epsilon_e \approx 2$ is the permittivity of the ions. It is found that the measured decrements of the NaCl solutions are much larger than predicted by the mixture relation (eq 10), e.g. $\epsilon_B = 78.7$ whereas $\epsilon(0) = 72.0 \pm 0.6$ at $c = 0.612$ mol/L. Hence at least one of the

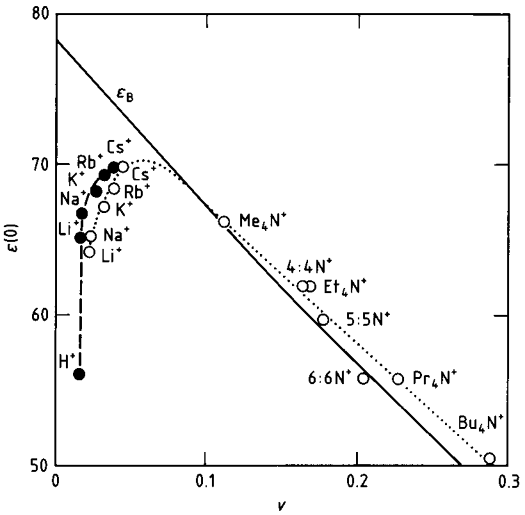

Figure 3. Extrapolated static permittivity $\epsilon(0)$ of 1 M aqueous solutions of some monovalent chlorides (closed circles[59]) and bromides (open circles[59,65]). X_4N^+ denotes the tetraalkylammonium ions, $Y{:}YN^+$ the azoniaspiroalkane ions.

aforementioned points (ii) or (iii) seems to play a significant role in the extrapolated static permittivity values of the NaCl solutions. The relative importance of the effect of kinetic depolarization and of structure saturation in electrolyte systems, however, is not clear at the present.[55−57] In Figure 3 $\epsilon(0)$ data of aqueous solutions of alkali chlorides and bromides as well as for bromides of large organic cations are presented. The extrapolated static permittivities for the solutions of tetraalkylammonium bromides and azoniaspiroalkane bromides rather exceed the corresponding ϵ_B values. This finding points at a slightly increased orientational polarizability of the water affected by the large ions. Such enhanced polarizability seems to be characteristic of hydrophobic hydration.[58] The $\epsilon(0)$ values of the solutions of small ions, however, decrease with decreasing cation radius r^+ (Figure 3). Globally, this behavior could result from both mechanisms under consideration. Due to the increasing Coulombic interaction, the extent of structure saturation, namely the preferential radial orientation of water dipoles in the cationic field, will increase with decreasing r^+. However, the particularly small $\epsilon(0)$ values for solutions containing protons call for an extra explanation since an unrealistically large extent of structure saturation effects would result from the extrapolated permittivty data. Empirically, the Onsager−Hubbard continuum theory of kinetic depolarization complies with the dielectric decrement $\delta\epsilon = \epsilon(0) - \epsilon_B$ of HCl and HBr solutions.[59] However, a successive shift of protons along hydrogen bonds[60] is assumed to be the dominating conductance mechanism rather than a hydrodynamic transport of charged species. The same arguments apply for the extrapolated static permittivities of sulfuric acid systems and their relation to the Onsager−Hubbard kinetic polarization deficiency,[61] since, in correspondence with water, a proton transfer mechanism along networks of associated molecules is assumed to exist in H_2SO_4.[62]

For slip boundary conditions at the ion surface the Onsager−Hubbard continuum theory predicts a kinetic dielectric decrement[63]

$$\delta\epsilon_{OH} = \frac{2}{3}\,\frac{\epsilon_v(0) - \epsilon_v(\infty)}{\epsilon_0\epsilon_v(0)}\,\sigma\tau_v = \frac{2}{3}F_{OH} \qquad (11)$$

directly proportional to σ and to the solvent relaxation time τ_v ($= \tau_w$ in aqueous systems). In eq 11, $\epsilon_v(0)$ and $\epsilon_v(\infty)$ denote the extrapolated low- and high-frequency permittivity, respectively. In Figure 4, $\delta\epsilon_{HO}$ data for solutions of $LiNO_3$ in different solvents are displayed as a function of F_{OH} in order to examine the potential relevance of the Onsager−Hubbard relation (eq 11). The various solvents cover a significant range of relaxation times ranging from about 8 ps (water, W) to 123 ps (*N*-methylformamide, MF). Obviously within this range of τ_v values there is an overall tendency in the $\epsilon_B - \epsilon(0)$ data to increase with F_{OH}. The experimental data, however, exceed the predictions of eq 11 for different amounts, indicating a specific structure of the different solvents.

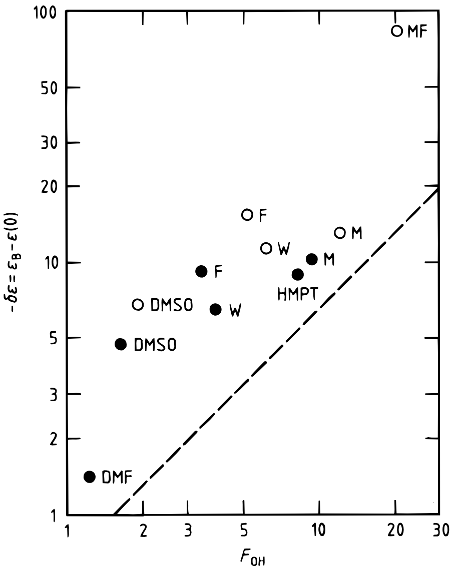

Figure 4. The negative dielectric decrement $\epsilon_B - \epsilon(0)$ displayed versus the quantity F_{OH} of the Onsager−Hubbard continuum model (eq 11) for solutions of lithium nitrate in various solvents (W, water; M, methanol; DMSO, dimethyl sulfoxide; F, formamide; MF, *N*-methylformamide; DMF, *N*,*N*-dimethylformamide; HMPT, hexamethylphosphoric triamide) at 25 °C.[66,67] Closed circles denote data from 1 molar solutions; open circles refer to a solute concentration of 0.5 mol/L. The dashed line represents eq 11.

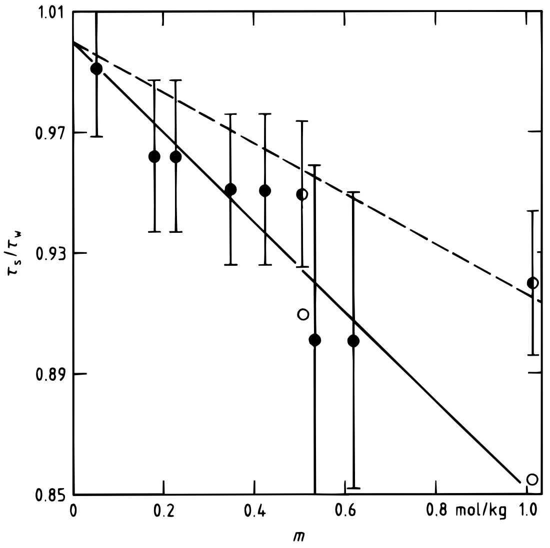

Figure 5. Relaxation time ratio τ_s/τ_w as a function of molal concentration m of solute for aqueous solutions of NaCl at 20 °C (●, this work; ○, ref 22) and at 25 °C (◐, refs 42 and 44).

Due to the comparatively short relaxation time of water, the Onsager−Hubbard static polarization deficiency for the aqueous NaCl is small ($\delta_{OH} = 0.58VmA^{-1}\sigma$, 25 °C). Nevertheless, consideration of an effect of kinetic depolarization noticeably alters the numbers $Z^+ + Z^-$ of apparently irrotationally bound water molecules per cation and anion. These numbers are based on the assumption that the effect of structure saturation around an ion consists of the predominantly preferential orientation of

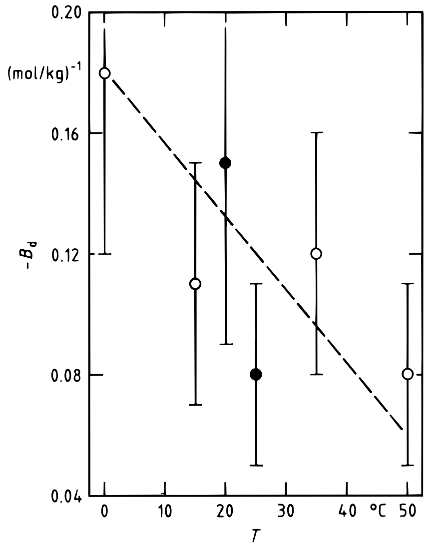

Figure 6. Negative relative molal shift of the principal dielectric relaxation time versus temperature T for aqueous solutions of NaCl (●, data at 20 °C and 25 °C from Figure 5; ○, unpublished results from the DPI).

the solvent dipole moment within the Coulombic field of the ion. An effect from a change of the average dipole moment of water molecules due to a reformation of the hydrogen network may be also included.[68] Here the numbers of saturated water molecules have been calculated according to the relation

$$Z^+ + Z^- = (v_B - v)/(c\phi_w) \tag{12}$$

where v_B denotes the apparent volume fraction of solute resulting from the Bruggeman relation (eq 10) and ϕ_w denotes the molar volume of water. $Z^+ + Z^- = 3.8$ is found if the extrapolated $\epsilon(0)$ values (Table 2) are used in eq 10, while $Z^+ + Z^- = 1.4$ results if the effect of kinetic depolarization is taken into account by inserting $\epsilon(0) + \delta\epsilon_{OH}$ in the Bruggeman relation. It is normally assumed that the effect of structure saturation in aqueous solutions of alkali chlorides is restricted to the cation. Hence our conclusion is that the structure saturation around a sodium ion corresponds with an equivalent of 1.4−3.8 apparently completely irrotationally bound water molecules per Na$^+$.

In Figure 5 the relaxation time ratio τ_s/τ_w of the NaCl solution is displayed as a function of the molal concentration of solute. Along with the τ_s/τ_w values by Zasetskii et al. at $c = 0.5$ and 1 mol/L, the data define a straight line which can be extrapolated back to pass through $\tau_s/\tau_w = 1$ at $m = 0$. The relative molal shift of the principal dielectric relaxation time, defined by the relation

$$B_d = \frac{1}{\tau_w} \lim_{m\to 0}\left(\frac{d\tau_s}{dm}\right) \tag{13}$$

is thus given by the slope of this line. $B_d = -(0.15 \pm 0.06)$ (mol/kg)$^{-1}$ is found at 20 °C, indicating a distinctly stronger decrease in the τ_s values on addition of salt than at 25 °C ($B_d = -(0.08 \pm 0.03)$ (mol/kg)$^{-1}$, Figure 5). The chloride ion includes weak effects of negative hydration.[4,44,53] Hence its hydration water reorientation time is slightly reduced with respect to τ_w. The opposite, however, is true for the sodium ion, the Coulombic field of which is sufficiently strong to impede the motions of adjacent water molecules, leading to effects of positive hydration.[4,44,53] Due to its finite residence time[64] in the hydration layer, the water affected by the sodium ion may nevertheless also tend to reduce the principal dielectric relaxation time τ_s of the solvent. There may also exist a layer of disturbed water molecules with negative hydration character around the dielectrically saturated shell of solvent surrounding the sodium ions. Obviously, the relative reduction in the dielectric relaxation time of the solutions increases with decreasing temperature (Figure 6), that is, with increasing degree of order of the water structure.

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