Static permittivity of water revisited: $\varepsilon$ in the electric field above $10^8$ V m$^{-1}$ and in the temperature range $273 \leq T \leq 373$ K

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Calculations are presented of the permittivity of water residing in conditions encountered in hydration shells. The present approach is applicable to water in high electric fields and in the whole range of temperature where it is liquid. Possible applications to various systems are mentioned. Static permittivity of aqueous solutions of exemplary salts is calculated and its comparison with experiment discussed in some detail.

1 Introduction

The electric fields above $10^8$ V m$^{-1}$ can be encountered, for example, in hydration layers arising when immersing in water the charged surfaces with surface (free) charge density $\sigma_0 \geq 10^{-3}$ C m$^{-2}$. Such charge densities can exist at the surfaces of flat$^1$ or spherical (mercury droplets)$^2$ metallic electrodes, oxides, for instance TiO$_2$ and RuO$_2$, at surfaces of proteins$^3,4$ and micelles as well as at internal surfaces of reverse micelles.$^5$ Such high local fields exist also around ions. It is convenient to treat single ions as point charges, and the fields they produce as the same as those which would be produced by concentric spherical surfaces with suitable charge densities.

The knowledge of the permittivity $\varepsilon$ is needed to evaluate some thermodynamic quantities of hydration shells. The quantities in question comprise entropy, the related electrocaloric effect, as well as the local electrostriction and electrostriction pressure in hydration shells.

Starting from the first half of the last century, different theories aimed at explaining the variation of the electric permittivity $\varepsilon$ of water with the field have been proposed (see ref. 9 for a review). Some papers reported the dependence of the permittivity $\varepsilon$ of water on the electric field strength (see, e.g., ref. 10 for a review). The measured dielectric constant depressions$^{10,11}$ caused in water by the addition of salts can be accounted for on the assumption that positive ions are surrounded by the first shells of water molecules exhibiting dielectric saturation. In refs. 12,13 the nonlinear dependence of the permittivity $\varepsilon$ of water on the distance from the centres of the ions was treated. In these papers calculations taken from ref. 14 were exploited. To calculate $\varepsilon$, one needs $\langle \cos \theta \rangle$. The statistical mean value of the cosine $\langle \cos \theta \rangle$ of the angle $\theta$ between the direction of the dipole moment $\mu$ of the water molecule and the direction of the electric field $E$ appeared to be expressed by the Langevin function. In ref. 14 the nonlinear dependence of the permittivity $\varepsilon$ of water on the electric field strength was analyzed at ambient conditions. In order to obtain the correct value of the permittivity decreasing with increasing field strength in the range where it falls off most abruptly, an adjustable parameter had to be introduced. Yet another approach to the dielectric constant of water (quantity independent of the electric field strength in the linear approximation) was developed by Eyring, who proposed a way of calculating the statistical mean value of $\langle \cos \theta \rangle$ for one of the two hypothetical species of water (solid-like) which, accidentally, was equivalent to the hyperbolic tangent function written in a mathematically different form. His theory describes well the dielectric constant of water in a wide range of temperatures, but in low electric fields ($E \leq 10^8$ V m$^{-1}$).

The interest focused recently on various hydrated systems, as exemplified above, calls for an approach that would lead to a description of the properties of hydration shells both in high electric fields and in sufficiently wide ranges of temperatures. Preferably, in contrast to some earlier work, it should not rely on adjustable parameters.

In this work, we calculate the values of the permittivity $\varepsilon(T,E)$ in high fields in the range $10^8 < E < 10^{11}$ V m$^{-1}$ in the whole temperature range of existence of the liquid phase of water. The statistical model approach applied here has originally been developed to explain the destroyed hydration structure of Ni$^{2+}$ ion in aqueous solution at elevated temperature and Sr$^{2+}$ ion at ambient temperature. Within our approach, the mean cosine $\langle \cos \theta \rangle$ value will appear to be expressed essentially by a Brillouin function. No adjustable parameter is needed. We shall mainly be interested in the permittivity of water in high fields in the range $273 \leq T \leq 373$ K, and the dielectric constant of pure water will be treated as known from the experiment.

As an immediate application, static electric permittivity $\varepsilon$ of aqueous solutions of exemplary salts will be calculated. Due to inherent experimental difficulties, which have not been circumvented yet, mainly the large electric conductivity of electrolytes, the agreement between any theory of mean $\varepsilon$ in aqueous salt solutions, including the present one, and experiment can be little more than estimated. It will be shown that according to such an estimation our results appear reasonable.

2 A statistical model of water permittivity

2.1 Linear approximation to the mean cosine

To relate the electric permittivity $\varepsilon$ with the dipole moment $\mu$ of a molecule one applies a statistical mechanical calculation leading to $\langle \cos \theta \rangle$, the mean cosine of the angle $\theta$. With no bounds imposed on the rotational motion of the dipole, it leads to an expression for $\langle \cos \theta \rangle$ in terms of the Langevin function, that provides correct predictions of the dielectric constant values for polar liquids with no hydrogen bonds.
this case, in the linear approximation,
\[
\langle \cos \theta \rangle = \frac{\mu E_{\text{On}}}{k T}
\]
(1)
where \(E_{\text{On}}\) is the Onsager local field\(^{17,18}\) and \(k\) denotes the Boltzmann constant. The Onsager field approximation is up to the present\(^{21}\) considered as one of the best when applied to classical dipole systems. The above eqn. (1) for \(\langle \cos \theta \rangle\) does not hold for liquids with hydrogen bonds.\(^{22,23,26}\) For water, at ambient conditions, to achieve agreement with experiment, \(\langle \cos \theta \rangle\) has been expressed\(^{23,24}\) as a Brillouin function \(B_2(\xi)\),\(^{19,20}\)
\[
B_2(\xi) = \tanh(\xi),
\]
(2)
\[
\xi = \frac{\mu E_{\text{On}}}{k T}
\]
(3)
corresponding to only two allowed orientations of the dipole moment \((I = 2)\) and then, in the linear approximation,
\[
\langle \cos \theta \rangle \cong \frac{\mu E_{\text{On}}}{k T} = \xi.
\]
(4)
The different behavior of hydrogen-bonded and other liquids is illustrated in Fig. 1. It is plotted after Cole\(^{25}\) with a straight line added, marked ONSAGER(2) to stress the two allowed orientations of the dipole when calculating \(\langle \cos \theta \rangle\) with the Brillouin function \(B_2\) for hydrogen-bonded liquids instead of the usual Langevin function. The latter case results in the straight line marked ONSAGER(\(\infty\)) to stress the infinite number of allowed dipole orientations which applies to the ordinary dipolar liquids. Fig. 1 makes it clear that the so modified Onsager model provides a good description of the dielectric properties of liquids associated by hydrogen bonds.

Physically, the model assumption of two allowed orientations of dipoles is based on the existence of hydrogen bonds in liquid water\(^{6,23}\) and the connection of the direction of the dipole moment of water molecule with the positions of protons (cf. Fig. 2) in the hydrogen bonds it is involved in. The external electric field \(E\) is related with the Onsager local field \(E_{\text{On}}\) as follows (cf. ref. 18 eqn. 5.52, p. 175 therein):
\[
E_{\text{On}} = \frac{\varepsilon(n^2 + 2)}{2\varepsilon + n^2} E,
\]
(5)
where \(n\) denotes the refraction index. For the flat geometry of the space distribution of the charges generating the field \(E\) we have
\[
E = \frac{\sigma}{\varepsilon_0} \quad \text{and} \quad \sigma = E E_{\text{On}},
\]
(6)
where \(\sigma\) is the total charge surface density and \(\varepsilon_0\) the permittivity of the vacuum. Substituting eqn. (6) to eqn. (5) we get
\[
E_{\text{On}} = \frac{n^2 + 2}{\varepsilon_0(2\varepsilon + n^2)} \sigma.
\]
(7)
Eqn. (7) can be applied to different geometries of the space charge distribution by a proper definition of \(\sigma\). For the spherical geometry \(E\) represents the Coulomb field
\[
E = \frac{q}{4\pi\varepsilon_0 r^2},
\]
(8)
where \(q\) is the elementary charge \((16 \times 10^{-19} \text{ C})\), \(r\) denotes reduced radius \(x = \rho(\varepsilon_0 E_{\text{On}})^{1/2}\) (\( \rho \) is the distance from the centre of the ion, \(Z\) the number of excess elementary charges on an ion) and we have
\[
\sigma = \frac{q}{4\pi x^2}.
\]
(9)

2.2 Two temperature-dependent factors

In the framework of our present approach the realizations of dipoles responsible for the high dielectric constant of water can be treated as due to simultaneous shifts of the proton positions\(^{16,23}\) as first suggested by Pauling.\(^{25}\) The two possible orientations \((I = 2)\) of water molecules linked by hydrogen bonds at room temperature are illustrated, very schematically, in Fig. 2a. At room temperature, the hydrogen bond energy \((20–25 \text{ kJ mol}^{-1})\) exceeds the thermal energy \(RT\) \((\approx 2.5 \text{ kJ mol}^{-1})\) by a factor of about ten. Hence, the very concept of

Fig. 1 Electric permittivity \(\varepsilon\) of dipolar liquids as a function of \(N_\mu^2/(3\varepsilon_0 k T)\). Circles denote experimental data, the straight lines values of \(\varepsilon\) calculated on the basis of the Onsager model: ONSAGER(\(\infty\)), calculated on applying Langevin function (with any orientation of dipole moment possible), ONSAGER(2), calculated on applying the Brillouin function (hyperbolic tangent) for only two possible orientations of dipole moment (see text). After ref. 26 with the straight line denoted ONSAGER(2) added by one of the present authors (cf. ref. 22).

Fig. 2 (a) Water molecules linked with hydrogen bonds, schematically. Arrows mark their dipole moments \(\mu\). Reorientation of the dipole moments \(\mu\) is due to the simultaneous shifts in the proton positions. The figure illustrates the fact that in water at ambient temperature only two orientations of a dipole moment are allowed \((I = 2)\). (b) Freely rotating water molecules at very high temperatures (see text), schematically. Their dipole moments \(\mu\) can take arbitrary orientations in space \((I = \infty)\).
two possible orientations of water dipoles at ambient conditions, leading to eqn. (2), seems to be justified and not to be a mere empirical finding.

At very high temperatures, in which the thermal energy becomes comparable to the hydrogen bond energy (T ≈ 3000 K, RT ≈ 25 kJ mol⁻¹) most of the hydrogen bonds should be broken (Fig. 2b) and dipoles could rotate freely (I = ∞), which induces a behaviour described by the Langevin function L(Ξ). In this context it is natural to seek for an interpolation scheme between the two extremes of tanh(Ξ), corresponding to I = 2, and L(Ξ), corresponding to I = ∞, which represent the upper bound and the lower bound of ⟨cos θ⟩, respectively. It is conceivable that in intermediate temperature range part of hydrogen bonds is disrupted, which can be treated as leading to an intermediate number I of probable directions of the dipole moments lying between two extremes: 2 < I < ∞. In this way, two temperature-dependent factors appear in the permittivity of H₂O. The first one is related to the fact that the argument of the function defining ⟨cos θ⟩ is temperature-dependent. Indeed, Ξ represents the energy of the dipole μ in the field E expressed in units of kT. The second factor arises from the fact that H₂O molecules are hydrogen-bonded. With rising temperature the latter are subsequently broken, which leads to a gradual growth of the number I. It will be shown below that the knowledge of the number I is needed to choose a proper function defining the statistical mean value ⟨cos θ⟩ of cos θ. Note, however, that unlike our basic model assumption of two allowed orientations of dipoles at room temperature, the concrete form of statistics ruling the orientations of dipoles at higher temperatures leading to the higher order Brillouin functions B₁ described below represents only one of the possible ways of interpolation.

2.3 Dielectric constant and Brillouin function in an approximation in the field variable E

The value of ⟨cos θ⟩ for an arbitrary number I of orientations of a dipole is expressed by the Brillouin function¹⁹,²⁰

\[ B_I(\Xi) = \frac{I + 1}{I - 1} \coth \frac{I\Xi}{I - 1} - \frac{1}{I - 1} \coth \frac{\Xi}{I - 1} \]  

(10)

where Ξ is defined in eqn. (3). The Brillouin functions are known in the physics of magnetism, similarly as the Langevin function L(Ξ) introduced for the first time in the theory of paramagnetism. The form of L(Ξ) is obtained from the Brillouin function B₀(Ξ) in the limit (I → ∞). For small values of the argument Ξ the function B₀(Ξ) can be expanded into the power series:

\[ B_0(\Xi) = \Xi - \frac{\Xi^3}{4} + \frac{\Xi^5}{32} - \cdots \]  

(11)

Only the first term in the expansion, the linear term b₀(Ξ), is taken into account when one looks for the dielectric constant. The coefficient b₀(I) and the mean number of orientations I of the dipole moment are interrelated as (cf. eqn. (11)),

\[ b(I) = \frac{I + 1}{3(I - 1)}, \]  

(12)

or inversely

\[ I = \frac{3b + 1}{b - 1}. \]  

(13)

The relation between the permittivity ε and the electric field strength is, according to the Onsager field approximation,¹⁷,¹⁸ expressed as (cf. refs. 16 and 23):

\[ \frac{ε - n^2}{ε} = \frac{N₀^2μ(n^2 + 2)}{3nv} \langle \cos θ \rangle, \]  

(14)

where v is the molar volume, N₀ the Avogadro number and \( \langle \cos θ \rangle = B₁(\Xi); \)

for \( I = 2 \)

\[ \langle \cos θ \rangle = \tanh(\Xi); \]  

(16)

and from eqns. (7) and (3)

\[ \Xi = \frac{σμ(n^2 + 2)}{2kT_0(e^n + n^2/2)}. \]  

(17)

The numerical value b(∞) = 1/3, in the theory of permittivity based on the Onsager approximation of local field.¹⁷,¹⁸ E₀ν follows from the assumption that all orientations of the dipoles are allowed for and are equally probable (I = ∞), and one arrives at an expression for the dielectric constant (cf.,¹⁷ p. 178, eqn. (5.67) therein):

\[ \frac{3(e - n^2)(2ε + n^2)}{ε(n^2 + 2)^2} = \frac{1}{3\omega v kT}, \]  

(18)

where b(∞) = 1/3. According to our proposed interpolation scheme,¹⁶,²¹ for small electric fields (E ≈ 10⁵ V m⁻¹), starting from the Brillouin function instead of the Langevin function, one arrives (cf. eqn. (11)) at an analogous expression for the dielectric constant ε at a given temperature T and the number density N₀/v, are known from experiment. Note that b(I) must fulfil the inequality:

\[ \frac{1}{3} \leq b(I) \leq 1. \]  

(20)

The empirical fact that the low-field dielectric constant data of water in the temperature range 273 ≤ T ≤ 373 K do indeed lead to the values for the coefficient b(I) fulfilling, in a good approximation, inequality (20) confirms the possibility of application of our interpolation scheme. If the experimental data are such that b(I) takes values leading to non-integer values of I (cf. eqn. (13)), the function B₄(Ξ) should be treated as defined by eqn. (10).

2.4 Results of the calculations

2.4.1 Coefficient b(I) and number I for water in the temperature range 273 ≤ T ≤ 373 K. Table 1 presents the physical quantities involved in eqn. (19) needed to find the value of b(I). The second column of Table 1 gives the values of the refraction index at T = 373 K do indeed lead to the values for the coefficient b(I) fulfilling, in a good approximation, inequality (20) confirms the possibility of application of our interpolation scheme. If the experimental data are such that b(I) takes values leading to non-integer values of I (cf. eqn. (13)), the function B₄(Ξ) should be treated as defined by eqn. (10).

2.4.2 Calculation of the permittivity ε = ε(T, E) in fields E > 10⁵ V m⁻¹ at temperatures in the range 273 ≤ T < 373 K. Permittivity ε of water has been calculated on the basis of eqn. (14). Expressing ⟨cos θ⟩ in this equation by the function given by eqn. (10), this time without the approximation linear in the field, we obtain

\[ \frac{ε - n^2}{ε} = \frac{N₀^2μ(n^2 + 2)}{3nv} \left[ \frac{I + 1}{I - 1} \coth \frac{I\Xi}{I - 1} - \frac{1}{I - 1} \coth \frac{\Xi}{I - 1} \right]. \]  

(21)
the plot of $E$ for each temperature reveals an abrupt fall at about $10^9 \text{ V m}^{-1}$. Similarly, the dependence of the permittivity $\varepsilon$ on temperature $T$ and the reduced distance from the centre of the ion $x$ and $\varepsilon = \varepsilon(T,x)$ has been found on the basis of eqn. (21) with eqn. (23) taken into account. This is shown in Fig. 4. The reduced radius $x$ measured from the centre of an ion is related to the field strength $E$ by the Coulomb formula (eqn. (8)). Large distances from the centres of ions (values of $\varepsilon$) correspond to small field strengths and vice versa. For large values of $x \approx 6 \text{ Å}$ the plots of the permittivity $\varepsilon$ in Fig. 4 tend, as before, to the values of the dielectric constant given in the fourth column in Table 1. For small values of $x$ the plot of $\varepsilon$ approaches the temperature-independent state characteristic of dielectric saturation with $\varepsilon \rightarrow \varepsilon^*$. For $x \approx 2.2 \text{ Å}$ an abrupt fall of $\varepsilon$ is apparent. In both the above calculations the calculated quantity $\varepsilon$ is involved in the corresponding equations implicitly, i.e., on the l.h.s. of the equation and on its r.h.s in the argument of the expression for $\langle \cos \theta \rangle$. For temperatures in the range $273 < T < 373 \text{ K}$ our results are presented in parallel in the figures and in Tables 2–5. For those who might wish to compare our results with the earlier literature data given at $25^\circ \text{C}$, the plots for $T = 298 \text{ K}$ are specified by dashed lines in Fig. 3 and Fig. 4. The calculated data of $\varepsilon$, $E$ and $x$ for $298 \text{ K}$ are collected in Table 3. The overall shape of our plots (dashed lines) agrees with those of the authors mentioned above.

Note that in our calculations we have considered the nonlinear effects due to only the permanent moments of the water molecules. No corrections for electrostriction and for deviation from linear dependence of the induced moments of molecules on the applied field have been taken into account. In this work, the induced moments are included in a linear approximation in the Onsager field $E_{\text{On}}$ based on the Lorentz–Lorenz equation. The huge electrostriction in high fields can make the permittivity larger due to a higher density. A general discussion of nonlinear corrections to induced dipole moments can be found in literature (ref. 18, p. 309, ref. 30, p. 206).

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The quantity $Z$ given in eqn. (3), with the notation introduced in eqn. (5) can be written as

$$Z = \frac{\mu E \varepsilon (n^2 + 2)}{kT \Delta \varepsilon n^2} ,$$

or, introducing the Coulomb field (eqn. (8)):

$$Z = \frac{e \mu n^2 + 2}{4\pi\varepsilon_0 e^2 kT 2\varepsilon n^2} .$$

Shown in Fig. 3 are the calculated dependencies of the permittivity $\varepsilon$ on temperature (in the range of temperature in which H$_2$O is liquid), and the electric field strength $E = \varepsilon(T,E)$. This plot is obtained on the basis of eqn. (21) with eqn. (22) taken into account. For small values of $E < 10^9 \text{ V m}^{-1}$, the corresponding values of the permittivity $\varepsilon$ at given temperatures tend to the values of the dielectric constant given in the fourth column in Table 1. The plot of $\varepsilon$ in the Fig. 3 reveals the temperature-independent state of dielectric saturation achieved in high fields $E > 10^{10} \text{ V m}^{-1}$. In this limit the permittivity $\varepsilon$ approaches the square of the value of the refraction index $n^2$. As $E$ increases, $n^2$ increases towards the limit $n^2 = \varepsilon$. For values of $\varepsilon$ in the range $273 < T < 373 \text{ K}$ our results are presented in parallel in the figures and in Tables 2–5. For those who might wish to compare our results with the earlier literature data given at $25^\circ \text{C}$, the plots for $T = 298 \text{ K}$ are specified by dashed lines in Fig. 3 and Fig. 4. The calculated data of $\varepsilon$, $E$ and $x$ for $298 \text{ K}$ are collected in Table 3. The overall shape of our plots (dashed lines) agrees with those of the authors mentioned above.

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### Table 3

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### 3 Molar decrement δ in the dielectric constant of water caused by ions at 298 K

The decrease of E in 1 molar aqueous solution (1 M aq. sol.) with respect to pure water is termed molar dielectric decrement δ. Now, from our calculated results for E at 298 K presented in Table 3 and plotted in Figs. 3 and 4, the molar decrement δ

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shall be found. It is known from experiment (cf. refs. 10,11,31) that for 1:1 salts the permittivity \( \varepsilon \) in 1 M aq. sol. decreases some 10–17.5% with respect to that of pure water. The diminution of the dielectric constant of water for 1:2 and 1:3 salts in 1 M aq. sol. is more significant.\(^{11}\) We calculate the permittivity of 1 M aq. sol. of LiCl, MgCl\(_2\) and LaCl\(_3\), on the assumption of infinite dilution. The \( \varepsilon \) of water will be calculated as a weighted sum of the permittivity of water in different phases present in the solution. One of them is the fully orientationally ordered and compressed phase \( A^{23,32} \) of water occurring in the first hydration shell of cations. Another one is the partly orientationally ordered and not compressed phase \( B^{3,32} \) in the second hydration shells of cations and the first hydration shells of anions. Yet another phase represents free water far from the ions. In Table 6 some data for ions and their hydration shells are collected. The molar volume \( (V_i = M_i/\rho) \) of water in the first hydration shell (the subscript \( i \) concerns the first hydration shell, \( ii \)–the second one, the subscript 1 denotes water, 2–salt) has been calculated on the basis of the data of the density of water in the high electric field acting in this shell (ref. 23, Tables 4–6, or ref. 33, Table 1). By multiplication of the molar volume of water in the first hydration shells \( V_i \) and the second ones \( V_{ii} \) by the coordination numbers of the first (second) hydration shell \( h_i \) and \( h_{ii} \), respectively, the values of \( V_i \) and \( V_{ii} \)–the volumes of water per mole of ions contained in their first and second shells, respectively, have been obtained.

Table 7 gives some data for 1 M aq. sol. of LiCl, MgCl\(_2\) and LaCl\(_3\). The intrinsic molar volume \( V^f \) is determined by

\[
V^f = (V^i)^k + l(V^{ii})^k, \quad l = 1, 2, 3, \quad (24)
\]

for 1:1, 1:2 and 1:3 salts, respectively, with the superscript \( k \) denoting the cation and \( a \) the anion. The volume of a single ion amounts to \( (4\pi/3)R^3 \), where \( R \) is the Goldschmidt ionic radius\(^{10} \) (cf. Table 6). The number \( n_i \) of moles H\(_2\)O in 1 litre of the 1 M aq. sol. has been obtained from the density of the solution \( \rho \) (in g cm\(^{-3}\)):\(^{34}\)

\[
n_i = (1000\rho - M_2)/M_1, \quad (25)
\]

where \( M_2 \) is the molar weight of a salt (Table 7) and \( M_1 = 18.0153 \) (in g) is the molar weight of H\(_2\)O.

Fig. 5 shows the volumes (in cm\(^3\)) of different phases of H\(_2\)O in 1 M aq. sol. of salts. The sum of the intrinsic volume \( V^f \), H\(_2\)O in the first \( (V^i) \) and the second \( (V^{ii}) \) shells about cations, H\(_2\)O in the shells about anions \( (V^{a}) \) and free water \( (V^d) \) amounts to 1000 cm\(^3\):

\[
V^f = 1000 - V^c - V^d, \quad (26)
\]

where

\[
V^c = V_i + V_{ii} + V^{a}. \quad (27)
\]

In order to calculate \( \varepsilon' \) (molar volume of free water) one needs to know \( n^f \)–the number of moles of H\(_2\)O contained in the volume \( V^f \). This number amounts to

\[
n^f = n_i - h_i^a - h_{ii}^a - h_i^c \quad (28)
\]

and we obtain

\[
\varepsilon' = V^f/n^f. \quad (29)
\]

One can see in Table 7 that the molar volume of free water \( \varepsilon' \) in solutions of MgCl\(_2\) and LaCl\(_3\) is larger, but in a solution of LiCl it is only slightly larger than the molar volume \( \varepsilon \) of the ordinary pure bulk water at 298 K (see Table 1). The dielectric constant \( \varepsilon' \) of the free water is calculated on the basis of eqn. (19) by putting \( \nu = \varepsilon' \). The mean permittivity of a dilute solution can be calculated as follows:

\[
\varepsilon_{\text{sol}} = \frac{\varepsilon_1 V_1^f + \varepsilon_2 V_2^f + \varepsilon_3 V_3^f + \varepsilon' V^f}{1000} \quad (30)
\]

The values of the permittivity \( \varepsilon_{\text{sol}} \) for 1 M aq. sol. of the salts under investigation calculated on the basis of eqn. (30) are given in Table 7. The dielectric constant of pure water differs from that of the solution of a given salt. As already noted, this difference is characterized by a number termed dielectric decrement \( \delta \). The molar dielectric decrement is defined as the difference between the permittivity of water \( (\varepsilon = 78.4 \text{ at } T = 298 K) \) and the permittivity of the 1 M aq. sol. (eqn. 30). The values of the molar decrement, \( \delta_{\text{sol}} \), calculated in this work are given in the last row in Table 7. We have found, in agreement with the knowledge based on experiment, that for the solution of 1:1 salts \( \varepsilon \) is lower by about 8–14,\(^{10}\) and the diminution of the dielectric constant of water for 1:2 and 1:3 salts in 1 M aq. sol. is more significant.\(^{11}\) However, we have found that in contrast to the 1 M aq. sol. of 1:1 salts the 1 M aq. sol. of 1:2 and 1:3 salts cannot be treated as dilute ones. It is apparent in Fig. 5. For the solutions of 1:2 (MgCl\(_2\)) and 1:3 (LaCl\(_3\)) salts, the volume \( V^f \) of free water calculated on the assumption that all ions are isolated from each other is significantly lower than that for 1:1 salts (LiCl). However, it is well known that for non-dilute solutions, contact ion pairs are formed, leading to a change in the distance ion–H\(_2\)O as well as the coordination number \( h_i \).\(^{35,36}\) Hence, the parts of Fig. 5 concerning MgCl\(_2\) and LaCl\(_3\) are credible mostly in this respect that they indicate the non-dilute nature of the respective solutions, as noted above.

### Table 7

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<th>LaCl(_3)</th>
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**This journal is © The Owner Societies 2004 Phys. Chem. Chem. Phys., 2004, 6, 1332–1339**
The values of \( \epsilon \) are affected more strongly for 1:2 and 1:3 salts in 1 M aq. sol. to about 10% of \( \epsilon \). The values of \( \epsilon \) extrapolated from measurements at high frequencies and for very low concentrations (cf. discussion in ref. 37). Hence, as already noted, it should be accepted that the experimental values of \( \epsilon \) for solutions of 1:1 salts, amount to about 10% of \( \epsilon \), and that the dielectric constant of water is affected more strongly for 1:2 and 1:3 salts in 1 M aq. sol. The values of \( \epsilon \) that have been calculated for aqueous solutions for exemplary salts LiCl, MgCl\(_2\), and LaCl\(_3\) are collected in Table 7. Yet other quantities calculated in this work are the volume fractions of water residing in the 1st or 2nd hydration shells of cations and anions with respect to the total amount of water in 1 M aq. sol. (Fig. 5). It is clear from the figures that 1 M aq. sol. of 1:1 salts cannot be treated on equal footing with those for 1:2 and 1:3. Consequently, the calculated quantities \( \epsilon_{cal} \) and \( \delta_{cal} \) in Table 7 for MgCl\(_2\) and LaCl\(_3\) (but not for LiCl), as corresponding to 1 M aq. sol., should be taken with great care.

5 Summary

We extend a model approach to permitivity in high electric field of water to cover the whole temperature range of its existence as a liquid under atmospheric pressure. Detailed calculated values of permittivity \( \epsilon \) are presented in Tables 2-5 and in Figs. 3 and 4. As remarked in the Introduction, they can form a basis to find various physical properties of hydration shells. A fragmentary application of this statistical model has earlier been presented by the present authors.\(^\text{16,23}\) At some high values of temperature approaching the critical region, the destroyed hydration structure of the Ni\(^{2+}\) ion in aqueous solution has been explained\(^\text{16,16}\) in this way. One of the quantities suitable for comparison with experiment is the molar decrement \( \delta \) of the dielectric constant in aqueous solutions of 1:1 salts. As discussed above, such electrolytes (in contrast to the 1 M aq. sol. of 1:2 and 1:3 salts) can be treated as diluted ones. The calculations (performed with no use of adjustable parameters) of \( \delta_{cal} \) at 298 K for an exemplary system, 1 M aq. sol. of LiCl, leads to a reasonable agreement with experiment.

References

12 J. Padova, J. Chem. Phys., 1963, 39, 1552. Fig. 1 therein.


