

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

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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 $\sigma_0 \geq 10^{-3} \text{ C m}^{-2}$. Such charge densities can exist at the surfaces of flat¹ or spherical (mercury droplets)² metallic electrodes, oxides, for instance TiO_2 ³ and RuO_2 ,⁴ at surfaces of proteins⁵⁻⁷ and micelles as well as at internal surfaces of reverse micelles.⁸ 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 ϵ 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 ϵ of water with the field have been proposed (see ref. 9 for a review). Some papers reported the dependence of the permittivity ϵ 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 ϵ 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 ϵ , one needs $\langle \cos \theta \rangle$. The statistical mean value of the cosine $\langle \cos \theta \rangle$ of the angle θ between the direction of the dipole moment μ of the water molecule and the direction of the electric field E ¹⁴ appeared to be expressed by the Langevin function. In ref. 14 the nonlinear dependence of the permittivity ϵ 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,¹⁴ 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,¹⁵ 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 theory¹⁵ describes well the dielectric constant of water in a wide range of temperatures, but in low electric fields ($E \approx 10^3 \text{ V m}^{-1}$).

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 $\epsilon(T, E)$ in high fields in the range $10^8 \text{ V m}^{-1} < E < 10^{11} \text{ V m}^{-1}$ 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.¹⁶ 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 $273 \leq T \leq 373 \text{ K}$, and the dielectric constant of pure water will be treated as known from the experiment.

As an immediate application, static electric permittivity ϵ 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 ϵ 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 ϵ with the dipole moment μ of a molecule one applies a statistical mechanical calculation leading to $\langle \cos \theta \rangle$, the mean cosine^{17,18} of the angle θ . 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,^{19,20} that provides correct predictions of the dielectric constant values for polar liquids with no hydrogen bonds. In

this case, in the linear approximation,

$$\langle \cos \theta \rangle = \frac{\mu E_{\text{On}}}{3kT}, \quad (1)$$

where E_{On} is the Onsager local field^{17,18} and k denotes the Boltzmann constant. The Onsager field approximation is up to the present²¹ 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} by a Brillouin function $B_2(\Xi)$,^{19,20}

$$B_2(\Xi) = \tanh(\Xi), \quad (2)$$

$$\Xi = \frac{\mu E_{\text{On}}}{kT} \quad (3)$$

corresponding to only two allowed orientations of the dipole moment ($I = 2$) and then, in the linear approximation,

$$\langle \cos \theta \rangle \cong \frac{\mu E_{\text{On}}}{kT} = \Xi. \quad (4)$$

The different behavior of hydrogen-bonded and other liquids is illustrated in Fig. 1. It is plotted after Cole²⁶ 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(∞) 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.

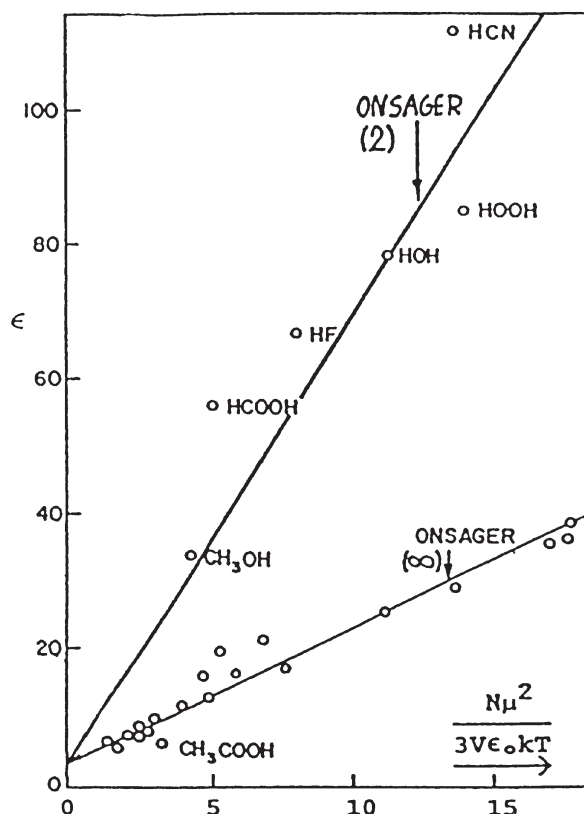


Fig. 1 Electric permittivity ϵ of dipolar liquids as a function of $N\mu^2 / (3V\epsilon_0 kT)$. Circles denote experimental data, the straight lines values of ϵ calculated on the basis of the Onsager model: ONSAGER(∞), calculated on applying Langevin function (with any orientation of dipole moment possible). 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).

Physically, the model assumption of two allowed orientations of dipoles is based on the existence of hydrogen bonds in liquid water^{16,23} 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_{On} as follows (cf. ref. 18 eqn. 5.52, p. 175 therein):

$$E_{\text{On}} = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} E, \quad (5)$$

where n denotes the refraction index. For the flat geometry of the space distribution of the charges generating the field E we have

$$E = \frac{\sigma}{\epsilon\epsilon_0} \quad \text{and} \quad \sigma = E\epsilon\epsilon_0, \quad (6)$$

where σ is the total charge surface density and ϵ_0 the permittivity of the vacuum. Substituting eqn. (6) to eqn. (5) we get

$$E_{\text{On}} = \frac{n^2 + 2}{\epsilon_0(2\epsilon + n^2)} \sigma. \quad (7)$$

Eqn. (7) can be applied to different geometries of the space charge distribution by a proper definition of σ . For the spherical geometry E represents the Coulomb field

$$E = \frac{q}{4\pi\epsilon\epsilon_0 x^2}, \quad (8)$$

where q is the elementary charge (16×10^{-20} C), x denotes reduced radius $x = r|Z|^{1/2}$ (r is the distance from the centre of the ion, Z the number of excess elementary charges on an ion) and we have

$$\sigma = \frac{q}{4\pi x^2}. \quad (9)$$

2.2 Two temperature-dependent factors

In the framework of our present approach the reorientations 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 ($20\text{--}25 \text{ kJ mol}^{-1}$) exceeds the thermal energy RT ($\approx 2.5 \text{ kJ mol}^{-1}$) by a factor of about ten. Hence, the very concept of

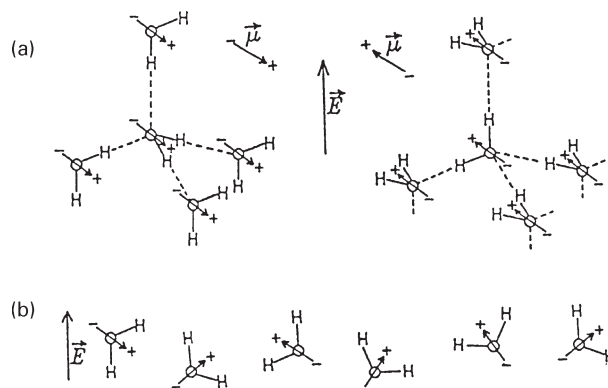


Fig. 2 (a) Water molecules linked with hydrogen bonds, schematically. Arrows mark their dipole moments μ . Reorientation of the dipole moments μ is due to the simultaneous shifts in the proton positions. The figure illustrates the fact that in water at ambient temperature only two orientations of a dipole moment are allowed ($I = 2$). (b) Freely rotating water molecules at very high temperatures (see text), schematically. Their dipole moments μ 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 ($T \approx 3000$ K, $RT \approx 25$ kJ mol⁻¹) most of the hydrogen bonds should be broken (Fig. 2b) and dipoles could rotate freely ($I = \infty$), which induces a behaviour described by the Langevin function $L(\Xi)$. In this context it is natural to seek for an interpolation scheme between the two extremes of $\tanh(\Xi)$, corresponding to $I = 2$, and $L(\Xi)$, corresponding to $I = \infty$, which represent the upper bound and the lower bound of $\langle \cos \theta \rangle$, 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: $2 < I < \infty$. In this way, two temperature-dependent factors appear in the permittivity of H₂O. The first one is related to the fact that the argument Ξ of the function defining $\langle \cos \theta \rangle$ 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 $\langle \cos \theta \rangle$ of $\cos \theta$. 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 B_I described below represents only one of the possible ways of interpolation.

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

The value of $\langle \cos \theta \rangle$ for an arbitrary number I of orientations of a dipole is expressed by the Brillouin function^{19,20}

$$B_I(\Xi) = \frac{I}{I-1} \coth \frac{I\Xi}{I-1} - \frac{1}{I-1} \coth \frac{\Xi}{I-1}, \quad (10)$$

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

$$B_I(\Xi) = \frac{I+1}{3(I-1)}\Xi - \frac{I^4-1}{45(I-1)^4}\Xi^3 + \dots \equiv b(I)\Xi - c(I)\Xi^3 + \dots \quad (11)$$

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

$$b(I) = \frac{I+1}{3(I-1)}, \quad (12)$$

or inversely

$$I = \frac{3b+1}{3b-1}. \quad (13)$$

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):

$$\frac{\varepsilon - n^2}{\varepsilon} = \frac{N^0 \mu(n^2 + 2)}{3\sigma v} \langle \cos \theta \rangle, \quad (14)$$

where v is the molar volume, N^0 the Avogadro number and

$$\langle \cos \theta \rangle = B_I(\Xi); \quad (15)$$

for $I = 2$

$$\langle \cos \theta \rangle = \tanh(\Xi) \quad (16)$$

and from eqns. (7) and (3)

$$\Xi = \frac{\sigma \mu(n^2 + 2)}{2kT \varepsilon_0(\varepsilon + n^2/2)}. \quad (17)$$

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

$$\frac{3(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} = \frac{1}{3} \frac{\mu^2 N^0}{\varepsilon_0 v k T}, \quad (18)$$

where $b(\infty) = 1/3$. According to our proposed interpolation scheme,^{16,23} for small electric fields ($E \approx 10^3$ 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 containing the factor $b(I)$ instead of $1/3$ present in eqn. (18):

$$\frac{3(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} = b(I) \frac{\mu^2 N^0}{\varepsilon_0 v k T}. \quad (19)$$

The numerical value of $b(I)$ can readily be found from eqn. (19) provided that the other quantities, and in particular the dielectric constant ε at a given temperature T and the number density N^0/v , are known from experiment. Note that $b(I)$ must fulfil the inequality:

$$\frac{1}{3} \leq b(I) \leq 1. \quad (20)$$

The empirical fact that the low-field dielectric constant data of water in the temperature range $273 \leq T \leq 373$ 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 $B_I(\Xi)$ 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 $273 \leq T \leq 373$ 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 taken from literature.^{27,28} The fourth column of Table 1 shows the values of the dielectric constant.²⁹ The fifth and sixth columns display the calculated values of $b(I)$ and I , respectively, at temperatures given in the first column. With these data at hand, our next task will be to calculate the permittivity ε in the high electric field at temperatures at which H₂O is liquid under atmospheric pressure.

2.4.2 Calculation of the permittivity $\varepsilon = \varepsilon(T, E)$ in fields $E > 10^8$ V m⁻¹ at temperatures in the range $273 \leq T < 373$ K. Permittivity ε of water has been calculated on the basis of eqn. (14). Expressing $\langle \cos \theta \rangle$ in this equation by the function given by eqn. (10), this time without the approximation linear in the field, we obtain

$$\frac{\varepsilon - n^2}{\varepsilon} = \frac{N^0 \mu(n^2 + 2)}{3\sigma v} \left[\frac{I}{I-1} \coth \frac{I\Xi}{I-1} - \frac{1}{I-1} \coth \frac{\Xi}{I-1} \right]. \quad (21)$$

Table 1 Values of the mean number I of allowed orientations of H₂O dipoles at temperature T /K and other quantities entering eqn. (19). n_D^T is the refraction index of water after refs. 27 and 28, v /cm³ is the molar volume of water after ref. 28, ϵ the water permittivity after ref. 29

T	n_D^T	v	ϵ	$b(I)$	I
273	1.33395	18.0182	87.9	1.003	1.996
283	1.33369	18.0207	83.96	0.993	2.010
293	1.33299	18.0477	80.20	0.984	2.024
298	1.33250	18.0687	78.40	0.980	2.031
303	1.33192	18.0940	76.60	0.975	2.038
313	1.33051	18.1566	73.17	0.967	2.052
323	1.32894	18.2334	69.88	0.959	2.066
333	1.32718	18.3231	66.73	0.950	2.080
343	1.32511	18.4249	63.73	0.942	2.095
353	1.32287	18.5381	60.86	0.934	2.120
363	1.32050	18.6625	58.12	0.926	2.125
373	1.31783	18.7980	55.51	0.918	2.140

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

$$\Xi = \frac{\mu E \epsilon (n^2 + 2)}{kT (2\epsilon + n^2)}, \quad (22)$$

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

$$\Xi = \frac{q}{4\pi\epsilon_0 x^2} \frac{\mu (n^2 + 2)}{kT (2\epsilon + n^2)}. \quad (23)$$

Shown in Fig. 3 are the calculated dependencies of the permittivity ϵ on temperature (in the range of temperature in which H₂O is liquid), and the electric field strength $\epsilon = \epsilon(T, E)$. This plot is obtained on the basis of eqn. (21) with eqn. (22) taken into account. For small values of $E < 10^8$ V m⁻¹, the corresponding values of the permittivity ϵ at given temperatures tend to the values of the dielectric constant given in the fourth column in Table 1. The plot of ϵ in the Fig. 3 reveals the temperature-independent state of dielectric saturation achieved in high fields $E > 10^{10}$ V m⁻¹. In this limit the permittivity ϵ

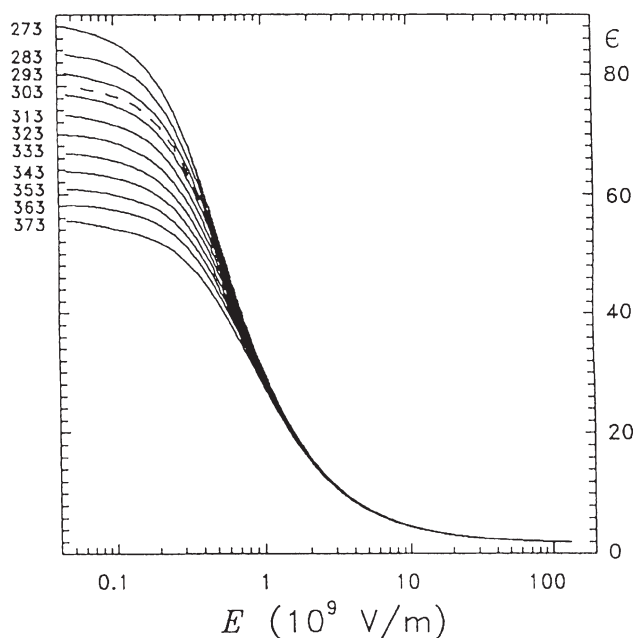


Fig. 3 Water permittivity $\epsilon = \epsilon(E)$ as a function of the field strength E within the temperature range $273 \leq T \leq 373$ K. The numbers on the left-hand side of the figure at the ends of the solid lines denote the absolute temperature for the respective lines. The dashed line is the plot of $\epsilon = \epsilon(E)$ for 298 K.

approaches the square of the value of the refraction index $\epsilon \rightarrow n^2$. Between these limiting values of the field, the permittivity ϵ for each temperature reveals an abrupt fall at about 10^9 V m⁻¹. Similarly, the dependence of the permittivity ϵ on temperature T and the reduced distance from the centre of the ion x , $\epsilon = \epsilon(T, x)$ 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 x) correspond to small field strengths and *vice versa*. For large values of $x \simeq 6$ Å the plots of the permittivity ϵ 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 ϵ approaches the temperature-independent state characteristic of dielectric saturation with $\epsilon \rightarrow n^2$. For $x \simeq 2.2$ Å an abrupt fall of ϵ is apparent. In both the above calculations the calculated quantity ϵ is involved in the corresponding equations implicitly, *i.e.*, on the lhs of the equation and on its rhs in the argument of the expression for $\langle \cos \theta \rangle$. For temperatures in the range $273 < T < 373$ 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^{12–14} given at 25 °C, the plots for $T = 298$ K are specified by dashed lines in Fig. 3 and Fig. 4. The calculated data of ϵ , E and x for 298 K are collected in Table 3. The overall shape of our plots (dashed lines) agrees with those of the authors mentioned above.^{12–14}

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_{On} based on the Lorentz–Lorenz equation.¹⁸ The huge electrostriction²³ 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).

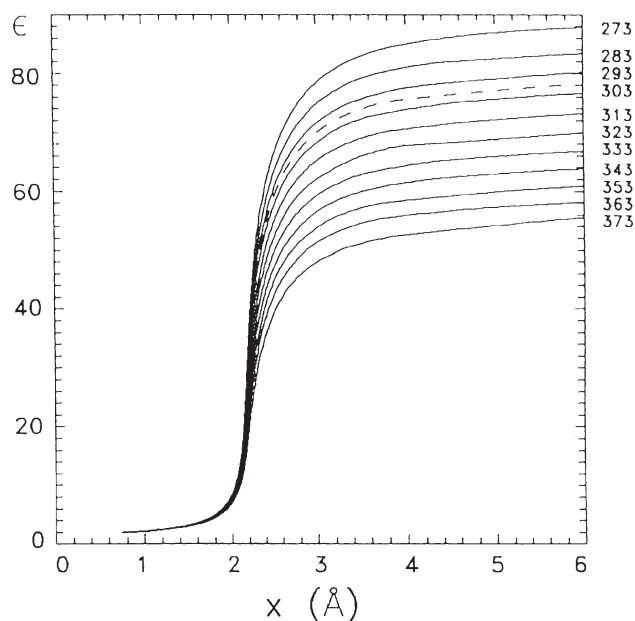


Fig. 4 Water permittivity $\epsilon = \epsilon(x)$ as a function of the reduced distance x from the centre of an ion in the temperature range $273 \leq T \leq 373$ K. The numbers on the right-hand side of the figure at the ends of the solid lines denote the absolute temperature for the respective lines. The dashed line is the plot of $\epsilon = \epsilon(x)$ for 298 K.

Table 2 Permittivity (ϵ) of water for electric field strength E or reduced radius (x) at 273, 283 and 293 K calculated on the basis of eqns. (21)–(23)

$T = 273 \text{ K}$			$T = 283 \text{ K}$		$T = 293 \text{ K}$	
ϵ	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$
2	0.743	130.07	0.745	129.36	0.749	128.16
2.25	1.020	61.43	1.025	60.83	1.028	60.48
2.5	1.202	39.80	1.203	39.75	1.206	39.57
3	1.428	23.45	1.430	23.45	1.431	23.39
4	1.669	12.89	1.670	12.89	1.671	12.87
5	1.797	8.91	1.799	8.89	1.800	8.88
6	1.875	6.81	1.880	6.78	1.881	6.775
7	1.933	5.49	1.934	5.49	1.937	5.48
10	2.030	3.49	2.032	3.48	2.033	3.48
15	2.102	2.17	2.104	2.16	2.105	2.16
20	2.138	1.57	2.140	1.57	2.141	1.57
25	2.160	1.23	2.162	1.23	2.164	1.23
30	2.177	1.01	2.182	1.01	2.184	1.005
35	2.196	0.847	2.202	0.847	2.208	0.843
40	2.218	0.731	2.227	0.724	2.237	0.718
50	2.283	0.552	2.305	0.511	2.329	0.530
55	2.331	0.481	2.365	0.468	2.401	0.454
60	2.396	0.417	2.446	0.401	2.502	0.383
65	2.485	0.358	2.560	0.338	2.650	0.315
70	2.609	0.302	2.730	0.276	2.892	0.246
72.5	2.694	0.273	2.853	0.244	3.085	0.210
75	2.799	0.246	3.020	0.210	3.387	0.167
77.5	2.939	0.215	3.265	0.174	3.982	0.117
79	3.046	0.196	3.465	0.152	4.915	0.045
80	3.130	0.184	3.691	0.132	—	—
81.5	3.294	0.163	4.183	0.101	—	—
83	3.509	0.141	5.512	0.057	—	—
86	4.451	0.084	—	—	—	—
87	5.430	0.056	—	—	—	—

Table 3 Same as Table 2, at 298, 303 and 313 K

$T = 298 \text{ K}$			$T = 303 \text{ K}$		$T = 313 \text{ K}$	
ϵ	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$
2	0.752	127.37	0.755	126.17	0.763	123.58
2.5	1.208	39.46	1.210	39.28	1.216	38.91
3	1.433	23.35	1.436	23.26	1.441	23.09
4	1.673	12.85	1.675	12.81	1.680	12.73
5	1.802	8.87	1.804	8.84	1.809	8.79
6	1.883	6.77	1.885	6.75	1.890	6.71
7	1.938	5.47	1.940	5.46	1.945	5.43
8	1.979	4.59	1.981	4.58	1.986	4.56
9	2.010	3.96	2.012	3.95	2.017	3.93
10	2.035	3.48	2.037	3.47	2.042	3.45
15	2.107	2.16	2.109	2.16	2.114	2.16
20	2.142	1.57	2.144	1.56	2.150	1.555
25	2.166	1.23	2.169	1.23	2.175	1.216
30	2.188	1.00	2.191	0.998	2.200	0.990
35	2.212	0.840	2.218	0.853	2.231	0.836
40	2.244	0.714	2.252	0.709	2.271	0.697
45	2.287	0.611	2.299	0.605	2.327	0.590
50	2.345	0.523	2.362	0.515	2.404	0.498
55	2.425	0.445	2.452	0.435	2.516	0.413
60	2.538	0.372	2.581	0.360	2.688	0.332
65	2.711	0.301	2.796	0.285	2.990	0.247
68	2.867	0.257	2.980	0.238	3.331	0.191
70	3.010	0.227	3.171	0.204	3.756	0.146
72	3.210	0.194	3.458	0.167	4.864	0.084
72.5	3.272	0.185	3.568	0.157	—	—
75	3.745	0.137	4.520	0.094	—	—
78	6.000	0.040	—	—	—	—

Table 4 Same as Table 2, for 323, 333 and 343 K

$T = 323 \text{ K}$			$T = 333 \text{ K}$		$T = 343 \text{ K}$	
ϵ	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$
2	0.772	120.71	0.782	117.63	0.794	114.18
2.5	1.223	38.48	1.230	38.00	1.239	37.46
3	1.447	22.89	1.454	22.66	1.463	22.40
4	1.686	12.64	1.693	12.54	1.701	12.42
5	1.815	8.73	1.822	8.71	1.830	8.41
6	1.896	6.67	1.902	6.62	1.910	6.57
7	1.951	5.40	—	—	—	—
8	1.992	4.53	1.999	4.50	2.007	4.46
9	2.023	3.90	—	—	—	—
10	2.048	3.43	2.054	3.41	2.062	3.38
15	2.120	2.13	2.126	2.12	2.135	2.10
20	2.156	1.55	2.164	1.54	2.173	1.52
25	2.183	1.21	2.193	1.20	2.204	1.18
30	2.211	0.980	2.224	0.969	2.240	0.956
35	2.246	0.814	2.265	0.801	2.287	0.785
40	2.294	0.683	2.322	0.667	2.355	0.648
45	2.361	0.573	2.403	0.553	2.455	0.530
50	2.457	0.477	2.523	0.452	2.609	0.423
55	2.601	0.387	2.715	0.355	2.877	0.316
57.5	—	—	2.862	0.305	3.109	0.259
60	2.841	0.297	3.077	0.253	3.516	0.194
62	—	—	3.345	0.207	4.265	0.1275
62.5	—	—	3.437	0.195	—	—
65	3.348	0.197	4.303	0.119	—	—
68	4.250	0.117	—	—	—	—

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

The decrease of ϵ 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 ϵ at 298 K presented in Table 3 and plotted in Figs. 3 and 4, the molar decrement δ

Table 5 Same as Table 2, for 353, 363 and 373 K

$T = 353 \text{ K}$			$T = 363 \text{ K}$		$T = 373 \text{ K}$	
ϵ	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$	$x/\text{\AA}$	$10^{-9}E/\text{V m}^{-1}$
2	0.806	110.68	0.820	107.02	0.845	100.79
2.5	1.249	36.88	1.259	36.27	1.275	35.39
3	1.472	22.13	1.482	21.83	1.493	21.51
4	1.710	12.29	1.720	12.16	1.730	12.00
5	1.838	8.51	1.848	8.42	1.858	8.33
6	1.919	6.51	1.928	6.44	1.939	6.37
8	2.016	4.415	2.025	4.38	2.035	4.34
10	2.071	3.35	2.080	3.32	2.091	3.29
15	2.144	2.09	2.153	2.07	2.165	2.05
20	2.183	1.51	2.194	1.49	2.209	1.47
25	2.217	1.17	2.231	1.155	2.253	1.13
30	2.257	0.941	2.278	0.923	2.311	0.897
35	2.314	0.767	2.345	0.747	2.397	0.715
40	2.396	0.626	2.444	0.602	2.530	0.562
45	2.520	0.593	2.602	0.472	2.757	0.420
50	2.724	0.388	2.885	0.346	3.256	0.271
52.5	—	—	3.139	0.278	3.930	0.177
53	—	—	3.209	0.263	4.200	0.154
55	3.131	0.267	3.617	0.200	—	—
57	—	—	4.700	0.114	—	—
57.5	3.579	0.195	—	—	—	—
60	5.091	0.092	—	—	—	—

shall be found. It is known from experiment (*cf.* refs. 10,11,31) that for 1:1 salts the permittivity ϵ 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, MgCl₂ and LaCl₃, on the assumption of infinite dilution. The ϵ 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^{23,32} 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 ($v_i = M_1/\rho_i$) 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, MgCl₂ and LaCl₃. The intrinsic molar volume V^j is determined by

$$V^j = (V^j)^k + l(V^j)^a, \quad l = 1, 2, 3, \quad (24)$$

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 radius¹⁰ (*cf.* Table 6). The number n_1 of moles H₂O in 1 litre of the 1 M aq. sol. has been obtained from the density of the solution ρ (in g cm⁻³):³⁴

$$n_1 = (1000\rho - M_2)/M_1, \quad (25)$$

where M_2 is the molar weight of a salt (Table 7) and $M_1 = 18.0153$ (in g) is the molar weight of H₂O.

Fig. 5 shows the volumes (in cm³) of different phases of H₂O in 1 M aq. sol. of salts. The sum of the intrinsic volume (V^j), H₂O in the first (V_i^k) and the second (V_{ii}^k) shells about cations, H₂O in the shells about anions (V_i^a) and free water (V^f) amounts to 1000 cm³,

$$V^f = 1000 - V^c - V^j, \quad (26)$$

where

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

Table 6 Properties of the ions. $R/\text{\AA}$: Goldschmidt ionic radius,¹⁰ h_i (h_{ii}): number of molecules in the first (second) hydration shell,^{35,36} v_i (v_{ii})/cm³: molar volume of water in the first (second) hydration shells based on data in refs. 23 or 33, V_i (V_{ii})/cm³ per litre of 1 molar solution: volume of water in the first (second) hydration shells, ϵ_i (ϵ_{ii}): permittivity of water in the first (second) hydration shells

Ions	Li ⁺	Mg ²⁺	La ³⁺	Cl ⁻
R	0.78	0.78	1.04	1.81
h_i	6	6	9.13	6.4
h_{ii}	—	12	13	—
v_i	15.04	10.03	10.04	18.05
v_{ii}	—	18.05	18.05	—
V_i	90.24	60.18	91.76	115.52
V_{ii}	—	216.60	235.20	—
ϵ_i	7.3	3.2	3.2	72.64
ϵ_{ii}	—	70.00	66.58	—

Table 7 Data for 1 molar aqueous solution of LiCl, MgCl₂ and LaCl₃. V^j/cm^3 intrinsic volumes (eqn. (24)), $\rho/\text{g cm}^{-3}$ density of a solution,³⁴ M_2/g are the molar weights of salts, n_1 the number of moles of H₂O in solution (eqn. (25)), V^c/cm^3 the volume of water in the shells about ions (eqn. (27)), V^f/cm^3 the volume of free water (eqn. (26)), n^f is the number of moles of H₂O contained in the volume V^f (eqn. (28)), v^f/cm^3 is the molar volume of the free water (eqn. (30)), ϵ^f is the permittivity of free water (eqn. (19)), $\epsilon_{\text{cal}}^{\text{sol}}$ is the calculated permittivity of solution (eqn. (30)), $\delta_{\text{cal}} = 78.4 - \epsilon_{\text{cal}}^{\text{sol}}$ is the calculated molar dielectric decrement

Salts	LiCl	MgCl ₂	LaCl ₃
V^j	16.16	31.12	47.72
ρ	1.0219	1.0729	1.2146
M_2	42.49	95.22	247.27
n_1	54.37	54.27	53.81
V^c	205.76	507.82	673.52
V^f	778.08	461.06	278.76
n^f	41.97	23.47	12.48
v^f	18.54	19.64	22.34
ϵ^f	77.64	73.47	64.66
$\epsilon_{\text{cal}}^{\text{sol}}$	69.5	66.0	59.05
δ_{cal}	8.9	12.4	19.35

In order to calculate v^f (molar volume of free water) one needs to know n^f —the number of moles of H₂O contained in the volume V^f . This number amounts to

$$n^f = n_1 - h_i^k - h_{ii}^k - h_i^a \quad (28)$$

and we obtain

$$v^f = V^f/n^f. \quad (29)$$

One can see in Table 7 that the molar volume of free water v^f in solutions of MgCl₂ and LaCl₃ is larger, but in a solution of LiCl it is only slightly larger than the molar volume v of the ordinary pure bulk water at 298 K (see Table 1). The dielectric constant ϵ^f of the free water is calculated on the basis of eqn. (19) by putting $v = v^f$. The mean permittivity of a dilute solution can be calculated as follows:

$$\epsilon_{\text{cal}}^{\text{sol}} = \frac{\epsilon_i^k V_i^k + \epsilon_{ii}^k V_{ii}^k + \epsilon_i^a V_i^a + \epsilon^f V^f}{1000}. \quad (30)$$

The values of the permittivity $\epsilon_{\text{cal}}^{\text{sol}}$ 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 δ . The molar dielectric decrement is defined as the difference between the permittivity of water ($\epsilon = 78.4$ at $T = 298$ K) and the permittivity of the 1 M aq. sol. (eqn. (30)). The values of the molar decrement, δ_{cal} , 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 ϵ 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 (MgCl₂) and 1:3 (LaCl₃) 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–H₂O as well as the coordination number h_1 .^{35,36} Hence, the parts of Fig. 5 concerning MgCl₂ and LaCl₃ are credible mostly in this respect that they indicate the non-dilute nature of the respective solutions, as noted above.

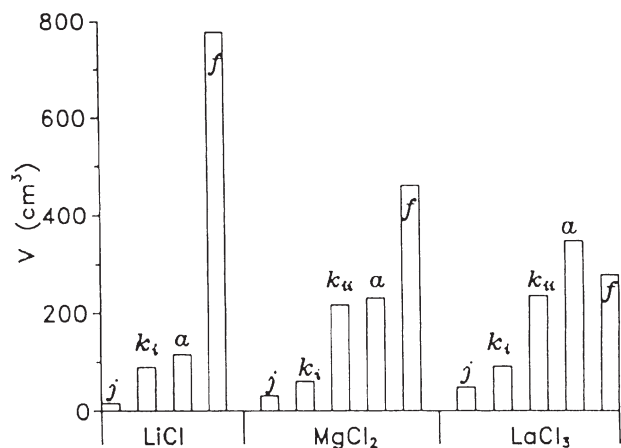


Fig. 5 Distribution of the volume of 1000 cm³ of 1 molar aqueous solution for LiCl, MgCl₂ and LaCl₃. *j* denotes the intrinsic volumes of cations and anions, *k_i* (*k_{ii}*) the volume of H₂O in the first (second) hydration shells of cations, *α* the volume of H₂O in the shells of anions, *f* the volume of the remaining free water.

4 Final remarks

We have presented our results for $\epsilon(E, T)$ and $\epsilon(x, T)$ in the form of tables and figures. The possibility of comparing these results with experiment comes from the measurement of the molar decrement δ of the permittivity ϵ of water when the salts are solved in water at 298 K. The experimental values of δ are known with a rather limited accuracy since the solutions of salts are good conductors of the electric current. The data of δ in 1 M aq. sol. of salts given in literature come from the values of ϵ 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 δ for solutions of 1:1 salts, amount to about 10% of ϵ , 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 δ that have been calculated for aqueous solutions for exemplary salts LiCl, MgCl₂ and LaCl₃ 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 by inspection that although 1 M aq. sol. of 1:1 salts could be treated as diluted ones, those of the 1:2 and 1:3 can not, since in the latter there is too little free water not engaged in the hydration shells left. Therefrom comes the warning 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 ϵ_{cal} and δ_{cal} in Table 7 for MgCl₂ and LaCl₃ (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 permittivity 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 ϵ 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.^{16,23} At some high values of temperature approaching the critical region, the destroyed hydration structure^{38,39} of the Ni²⁺ ion in aqueous solution has been explained¹⁶ in this way.

One of the quantities suitable for comparison with experiment is the molar decrement δ 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 δ_{cal} at 298 K for an exemplary system, 1 M aq. sol. of LiCl, leads to a reasonable agreement with experiment.

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