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The Dielectric Constant of Water at Very High Temperature and Pressure

(dielectric constant/relative permittivity/water/steam)

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Abstract

Pertinent statistical mechanical theory is combined with the available measurements of the dielectric constant of water at high temperature and pressure to predict that property at still higher temperature. The dielectric constant is needed in connection with studies of electrolytes such as NaCl-H₂O at very high temperature.
There is increasing interest in aqueous electrolytes at very high temperature and pressure in view of their role in hydrothermal transport of minerals and other geochemical phenomena and their potential interest in engineering applications. Theoretically interesting aspects of electrolyte theory also arise under these extreme conditions. As a foundation stone required for such electrolyte studies, the dielectric constant (relative permittivity) of water is needed at temperatures substantially higher than the range of present measurements. In this note an equation is developed, on the basis of dielectric theory as well as available experimental data, which is designed to yield the best available prediction of dielectric properties at temperatures above the range of measurement as well as to reproduce the best experimental data above 600 K within experimental uncertainty.

Quist and Marshall (1) addressed this same objective in 1965. Indeed we retain their choice of Kirkwood's theory and equation (2,3) but consider recent experimental data and modify the empirical expression for one term. Heger, Uematsu, and Franck (4,5) carried out an extensive program of measurement of the static dielectric constant of water at temperatures up to 823 K and pressures to 5 kbar. This is the primary experimental advance of recent years, although the measurements of Lukashov, et al. (6), which extend to 873 K for steam of moderate density, are also valuable. Uematsu and Franck (7) presented a purely empirical equation representing their measurements and those of others within the range of measurement, but its form is unsatisfactory for extrapolation to higher temperature. Their paper (7) should be consulted for the literature on earlier measurements.
The Kirkwood equation is

\[
\frac{(2D+1)(D-1)}{9D} = \frac{4\pi N_0 d}{3M} \left( \alpha + \frac{\mu}{3kT} g \right)
\]

where \(D\) is the dielectric constant, \(N_0\) is Avogadro's number, \(d\) the density, \(M\) the molecular weight, \(k\) the Boltzmann constant, \(\alpha\) the molecular polarizability, \(\mu\) the molecular dipole moment, and \(g\) is the Kirkwood correlation factor that accounts for nonrandom orientation of neighboring molecules. As the density decreases, \(g\) approaches unity, and the equation then applies rigorously to the ideal gas.

Since the Quist and Marshall paper there have been some improvements in the values of \(\alpha\) and \(\mu\); we adopt \(\alpha = 1.444 \times 10^{-24}\) and \(\mu = 1.84 \times 10^{-18}\) in cgs units as consistent with the best available data (8).

While the remaining quantity \(g\) is defined theoretically in terms of the degree of nonrandomness of orientation of neighboring dipole moments, it has not been calculated on a molecular basis to high accuracy. This can be understood since the calculation would involve all the details of the short-range interactions of water molecules. Thus it is preferable to evaluate \(g\) empirically over the range of measurement of \(D\).

Values of \(g\) were calculated from various dielectric measurements. The points on Fig. 1 show the values arising from Heger's measurements above 650 K and not exceeding 1000 bar pressure. For densities below 0.5 g cm\(^{-3}\) the points lie on a single straight line with no significant trend with temperature. The values of \(g\) from the measurements of Lukashov, et al. (6), are too scattered to be given significant weight; some points are close to the line shown while a few fall even below 1.0
and are certainly too low. At higher densities the curves were derived from the equation of Uematsu and Franck (7) which is an excellent representation of the experimental data in that range. There is a definite temperature dependence at high density. The equation

\[ g = 1 + 2.68 \cdot d + 6.69 \cdot d^5 \left[ \frac{(565/T)^{0.3}}{} - 1 \right] \]  

(2)
represents Heger's data up to 1000 bar with an average deviation of 2.2% and a maximum of 5.8%. For this particular range of temperature and density, Eqs. 1 and 2 represent a considerable improvement over the equation of Uematsu and Franck where deviations were as large as 15% at 773 K and 0.09 g cm\(^{-3}\) (where our deviation is 4.1%). At higher density the Uematsu and Franck equation is uncertain to less than 2.5% and the present equation has a similar uncertainty from 600 to 823 K.

The expression for \( g \) in Eq. 2 is empirical, except for the limit of 1 at low density, but from figure 1 it is apparent that the very simple linear portion below density of 0.5 is well substantiated. Even in the low-density range one might have expected some decrease in \( g \) with increasing \( T \), but a careful analysis of the deviations from Eq. 2 shows no significant trend with \( T \). Indeed a negative temperature derivative of as much as 0.001 in the linear parameter 2.68 would significantly disagree with the Heger measurements. Thus one has considerable confidence in using this expression for higher temperatures since the sensitivity of \( D \) to \( g \) diminishes with increase in \( T \). The last term, however, is more complex and, without a theoretical basis, its extrapolation to higher \( T \) is more questionable. Thus the results for densities greater than 0.5 g cm\(^{-3}\) are regarded as more uncertain than those for lower densities.
Table 1 gives the resulting values of the dielectric constant over a range of temperature and density of particular interest. In view of the simplicity of the equations and the ease of direct calculation, a very detailed or extensive table seems unnecessary. Figure 2 shows the general pattern predicted for even higher temperatures. The present equations predict values of $D$ as much as 10% greater than those of Quist and Marshall near 1000 K and 0.5 g cm$^{-3}$ but the percentage difference decreases considerably for either higher or lower densities or for lower temperatures. Since the information base for the present equation is considerably improved from that of Quist and Marshall, the present values should be uncertain by a percentage somewhat less than the difference between the two predictions. Thus the present values are estimated to be correct to about 3% from 600 to 850 K and to 5% through 1000 K and $d \leq 0.7$ g cm$^{-3}$. Above 1000 K estimates of uncertainty become more speculative, but the form of Eq. 1 is such that the result depends more on the well-known $\alpha$ and $\mu$ and less on the increase of $g$ above unity as $T$ increases. Thus it is not unreasonable to estimate a 15% uncertainty in $D$ to very high temperatures and for $d \leq 0.5$ g cm$^{-3}$. If values of $D$ are needed over a range in temperature extending from very high $T$ to below 600 K, then another equation must be used for the liquid below 600 K. This can be either the equation of Uematsu and Franck (7) or that of Bradley and Pitzer (9). Although the difference as small, the latter agrees more accurately with the values recommended by IUPAC (10). The present equation is valid for steam below 600 K.

Calculation of the Debye-Hückel parameter is, of course, one of the principal applications of the dielectric constant for electrolyte
solutions. The present results are being used for that purpose in studies on the system NaCl-H₂O over a wide range of temperature and the full composition range to saturation.

Acknowledgment

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REFERENCES

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Figure Captions

Figure 1. The Kirkwood g factor for H$_2$O at high T.

Figure 2. Calculated curves for the dielectric constant of H$_2$O at very high T.
Fig. 2
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