The Dielectric Constant of Deuterium Oxide

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In the calculation and interpretation of a variety of thermal effects in solution, such as heats of dilution and heats of solution, a knowledge of the dielectric constant of the solvent and its variation with temperature is essential. Quite recently Lange and others[1,2] have instituted an investigation of such phenomena in the case of inorganic salts in deuterium oxide, but in the discussion of their results they have been hindered by a lack of precise dielectric constant data for the solvent. In this paper are presented the results of measurements of the dielectric constant of heavy water over a temperature range from 0 to 100°. For purposes of comparison, and as a check on the experimental procedure, these are accompanied by the results of companion measurements made in exactly the same way on H_2O.

The deuterium oxide used in this study was obtained in sealed capsules from the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Oslo, and was characterized by $d^{20}_4 = 1.10537$, corresponding to a purity of 99.95%. The measurements were made by a resonance method, yielding absolute values of the dielectric constant, which has been used previously for measurement of the dielectric constant of H_2O.[3] The resonator, which can be very small and compact for work at high frequencies, is immersed completely in the medium to be measured, and its resonant frequency ν_x determined in terms of the frequency of a standard crystal. From this, and the frequency ν_0 of the same resonator determined in the same way in vacuo or immersed in any medium of known dielectric constant ϵ_0, the unknown dielectric constant ϵ_x is obtained from the relation[4]

$$\epsilon_x/\epsilon_0 = \nu^2_0/\nu^2_x \qquad (1)$$

in which, of course, ϵ_0 is unity for a vacuum.

In the present study two series of measurements were made, one on H_2O and one on D_2O. Each series involved the determination of the natural frequency of a small resonator immersed in the liquid at various temperatures between 0 and 100°, and in particular a very careful de-

termination of the frequency at 25°. These frequencies were between about 5.69×10^7 cycles per second ($\lambda = 5.28$ m.) at the upper end of the temperature range and about 4.55×10^7 cycles per second ($\lambda = 6.60$ m.) at the lower end. The same resonator was used in both series. This was a small spiral of heavy copper wire flattened by rolling and was unplated. It was suspended in the usual way by a fine thread in a jacketed glass vessel containing the liquid under measurement The D_2O was obtained in small sealed glass capsules. As soon as these were broken the contents were placed in the vessel with the resonator and stoppered up with a ground glass stopper in order to prevent contamination with H_2O from the atmosphere. It was only necessary to remove the stopper once or twice during the course of the measurements to adjust the resonator. On account of the possibility of systematic errors due to stray field effects care was taken to use an equal volume of liquid in the two sets of measurements.

The temperature was controlled by pumping water from a thermostatically regulated bath through the jacket surrounding the vessel. The temperature of this circulating water was measured as it entered and as it left the jacket. On the basis of a calibration with a standardized thermometer inserted into the vessel containing an amount of water equal to that used for the measurements it was possible to estimate the temperature of the liquid being measured from the "in" and "out" temperatures of the circulating water to 0.1° or better between 0 and 60° and 0.3° or better between 60 and 100°.

From the values of the natural frequency of a resonator in a given liquid at different temperatures we obtain at once by Equation 1 the relative values of the dielectric constant at those temperatures without a knowledge of the frequency of the resonator in vacuo, subject, however, to a small correction arising from the thermal expansion of the resonator itself. Thus the ratio ν_{25}^2/ν_t^2, where ν_t is the frequency of a resonator at temperature t and ν_{25} is its frequency at 25°, gives the ratio of the dielectric constant at temperature $t°$, ϵ_t, to that at 25°, ϵ_{25}, subject to

(1) Lange and Martin, Z. Elektrochem., **42**, 662 (1936).
(2) Birnthaler and Lange, ibid., **43**, 643 (1937).
(3) Wyman, Phys. Rev., **35**, 623 (1930).
(4) For the effects of conductivity see (3).

the correction. Each of the two sets of values of ν_{25}^2/ν_t^2 obtained in the two series of measurements on H_2O and D_2O is fitted adequately by a third degree equation.

For D_2O

$$\nu_{25}^2/\nu_t^2 = 1 - 4.582 \times 10^{-3} \, (t - 25) + 1.20 \times 10^{-5} \\ (t - 25)^2 - 2.7 \times 10^{-8} \, (t - 25)^3 \quad (2)$$

For H_2O

$$\nu_{25}^2/\nu_t^2 = 1 - 4.544 \times 10^{-3} \, (t - 25) + 1.17 \times 10^{-5} \\ (t - 25)^2 - 2.8 \times 10^{-8} \, (t - 25)^3 \quad (3)$$

In the case of D_2O, measurements were made at 24 different temperatures, roughly equally spaced, between 0.42 and 98.4°, and the mean deviation, regardless of sign, of the observed values of ν_{25}^2/ν_t^2 from the values given by Equation 2, is 0.00044. In the case of H_2O, measurements were made at 17 different temperatures between 0.52 and 98.7° and the mean deviation, regardless of sign, of the observed values from those given by Equation 3 is 0.00034.

We will now consider the effect of the thermal expansion of the resonator itself. This has not been done in previous studies by this method of the change of dielectric constant with temperature. Owing to the isotropic expansion of the copper, as the temperature is varied every dimension of the resonator will change by a fractional amount per degree equal to the linear coefficient of thermal expansion of the metal. The same will be true also of its inductance and its capacity (in a medium of fixed dielectric constant), each of these having the dimensions of length. Consequently its natural frequency, being equal to the reciprocal of the square root of the product of these two quantities, will itself also change, for a medium of fixed dielectric constant, by a fractional amount per degree equal to minus the linear coefficient of expansion of the metal. The change of frequency of the resonator due to thermal expansion between 25° and $t°$ is thus given by

$$\int_{25}^t \frac{d\nu}{\nu} = -\int_{25}^t \alpha \, dt$$

where α denotes the coefficient of expansion. For this reason values of the dielectric constant ratio ϵ_t/ϵ_{25} calculated from ν_{25}^2/ν_t^2 are in error and subject to correction by a factor $e^{-2\alpha(t - 25)}$. Neglecting second-order terms and higher we may therefore write

$$\epsilon_{25}/\epsilon_t = [\,1 - 2\alpha(t - 25)\,] \, \nu_{25}^2/\nu_t^2 \quad (4)$$

The coefficient of expansion of copper is close to 17.7×10^{-6} and the correction at a temperature of 100° amounts to 0.27%.

In order to test the validity of this correction, a test was made of the change with temperature of the natural frequency of a large brass resonator in air. The frequency of the resonator in air was found to be 8.7298×10^{-7} at 25° and 8.7197 at 98°. The difference between the two is 0.12%. If we neglect the change of dielectric constant of air with temperature and take the coefficient of thermal expansion of brass as 18.5×10^{-6}, the calculated value of the change of frequency is 0.14%. The agreement is sufficient to justify the use of the correction contained in Equation 4.

No attempt was made to redetermine the dielectric constant of H_2O at 25°. This was taken as 78.54,[3] and the dielectric constant of D_2O at 25° was determined in terms of this from the frequencies of the resonator in the two liquids at 25°. The value for heavy water thus obtained was 78.25. A later determination, made with a different resonator, gave the value 78.26, which agrees with the earlier value well within the experimental error.

Taking the values of the dielectric constant of D_2O and H_2O at 78.25 and 78.54, respectively, at 25°, and making use of Equation 4, with a value of 17.7×10^{-6} for α, we obtain finally

For D_2O

$$\epsilon = 78.25 \, [1 - 4.617 \times 10^{-3} \, (t - 25) + 1.22 \times 10^{-5} \\ (t - 25)^2 - 2.7 \times 10^{-8} \, (t - 25)^3] \quad (5)$$

For H_2O

$$\epsilon = 78.54 \, [1 - 4.579 \times 10^{-3} \, (t - 25) + 1.19 \times 10^{-5} \\ (t - 25)^2 - 2.8 \times 10^{-8} \, (t - 25)^3] \quad (6)$$

It may be seen from these results that the variation of dielectric constant with temperature is very nearly the same for H_2O and D_2O. Values of the expressions in brackets in these two equations calculated for the same temperatures differ by less than 0.1% between 0 and 50° and by no more than 0.14% at any temperature between 50 and 100°. The temperature coefficients $d\epsilon/dt$ and $1/\epsilon \, (d\epsilon/dt)$ agree to better than 1% over the entire temperature range. Values of $1/\epsilon \, (d\epsilon/dt)$ at various round temperatures are as follows

Temp., °C.	0	20	40
D_2O	−0.00470	−0.00463	−0.00457
H_2O	− .00466	− .00459	− .00454

Temp., °C.	60	80	100
D_2O	−0.00453	−0.00452	−0.00456
H_2O	− .00451	− .00452	− .00459

The only data in the literature with which to compare the results on D_2O are those of Lewis,

Olson and Maroney[5] which give for the ratio $\epsilon_{D_2O}/\epsilon_{H_2O}$ the values 0.990 at 25° and 0.982 at 10°. The values from the present investigation at these temperatures are 0.9963 and 0.9969, respectively. The present results on H_2O agree with the earlier published values based on the same method[3] to within ±0.15 in dielectric constant or better at all temperatures between 0 and 50°. Above 50° the discrepancy increases and becomes 0.57 at 100°, the new results being higher. This is probably due mainly to inaccuracies of temperature estimation at extreme temperatures in the earlier work. The temperature control and estimation was far better in the present study.

Åkerlöf[6,7] has shown that in many cases the logarithm of the dielectric constant varies linearly with temperature and has given for the dielectric constant of H_2O the following equation

$$\log_{10} \epsilon_{H_2O} = 1.9461 - 0.00205t$$

The present results for D_2O and H_2O may also be fitted with good approximation by a logarithmic equation with a somewhat different choice of constants

$$\log_{10} \epsilon_{H_2O} = 1.9446 - 0.00198t \quad (7)$$
$$\log_{10} \epsilon_{DH_2O} = 1.9433 - 0.00199t \quad (8)$$

Only at 0 and 100° do values calculated from these formulas for D_2O and H_2O differ from the observed values by as much as 0.15; over most of the temperature range the discrepancy is about half this or less.

According to the theory of Born[8,9] the expression for the heat of solvation of an ion contains as a factor representing the influence of the solvent the quantity

$$\left[1 - \frac{1}{\epsilon}\left(1 + \frac{T}{\epsilon}\frac{d\epsilon}{dT}\right)\right]$$

in which T is the absolute temperature and ϵ the dielectric constant of the solvent. In Debye's theory, at sufficiently low concentrations the integral heat of dilution of a strong electrolyte

(5) Lewis, Olson and Maroney, THIS JOURNAL, 55, 4731 (1933).
(6) Åkerlöf, ibid., 54, 4125 (1932).
(7) Åkerlöf, ibid., 58, 1241 (1936).
(8) Born, Z. Physik, 1, 45 (1920).
(9) Bjerrum and Larsson, Z. physik. Chem., 127, 369 (1927).

contains as a factor representing the influence of the solvent the quantity

$$\frac{1}{\epsilon}\left(1 + \frac{T}{\epsilon}\frac{d\epsilon}{dT}\right)$$

This latter quantity, which owing to the place it occupies in both theories plays an important role in the understanding of thermal phenomena in solutions, is quite sensitive to $d\epsilon/dt$. Values of it for H_2O and D_2O at various round temperatures calculated from Equations (5) and (6) are

Temp., °C.	0	20	40
D_2O	−0.00322	−0.00446	−0.00592
H_2O	− .00307	− .00429	− .00574

Temp., °C.	60	80	100
D_2O	−0.00695	−0.00755	−0.00854
H_2O	− .00682	− .00751	− .00868

From these figures, on the basis of purely electrostatic effects, which are the only ones considered in the two theories, we should predict only very small differences in heats of solvation and in heats of dilution for a given electrolyte in D_2O and H_2O. The recent studies of Birnthaler and Lange[2] on six strong electrolytes (NaCl, KBr, KF, $Ba(NO_3)_2$, $SrSO_4$, and $BeSO_4$) do in fact show that the heats of dilution in H_2O and D_2O approach one another very closely at low concentrations and appear to become equal. On the other hand, studies of Lange and Martin[1] on alkali halogenides show that the ionic heats of solvation in D_2O and H_2O differ by as much as 1%. Inasmuch as the factor in the Born theory varies by little more than 0.01% between H_2O and D_2O, it is clear that electrostatic effects are insufficient to explain the situation in regard to these heats.

Summary

Values of the dielectric constant and its temperature coefficient are reported for D_2O and H_2O between 0 and 100°. The dielectric constant of D_2O is slightly less than that of H_2O over the whole range; its temperature coefficient is everywhere very nearly the same. The bearing of the results on the problem of heats of solvation and heats of dilution of strong electrolytes is discussed.