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9.355 GHz complex permittivity of water from 1 °C to 90 °C

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Abstract. This paper reports the results of a systematic study of the 9.355 GHz complex permittivity of double-distilled, deionized water over the temperature interval from 1 °C to 90 °C in ~ 2 °C steps. A precision of $\sim 0.03\%$ and an accuracy of $\sim 0.1\%$ were achieved for both the permittivity ϵ' and the dielectric loss ϵ'' : $\epsilon'(T) = 43.789(18) + 1.4098(18)T - 3.008(26) \times 10^{-2}T^2 + 2.249(71) \times 10^{-4}T^3 - 2.33(85) \times 10^{-7}T^4 - 3.14(36) \times 10^{-9}T^5$; $\epsilon''(T) = 39.9615(91) - 1.77(20) \times 10^{-2}T - 3.350(13) \times 10^{-2}T^2 + 8.387(36) \times 10^{-4}T^3 - 8.470(42) \times 10^{-6}T^4 + 3.146(18) \times 10^{-8}T^5$ where T is in °C. It shows that the values of the thermodynamic parameters entropy (ΔS), enthalpy (ΔH), and free energy (ΔF) of activation are temperature dependent, contrary to previous reports. The temperature dependence of the relaxation time in this temperature interval is in good agreement with that reported in the literature. The values of the thermodynamic functions, calculated using the various pairs of α and ϵ_∞ values reported in the literature, agree within 1σ over most of the measurement temperature interval.

1. Introduction

Water is a relatively simple liquid. However, its simplicity is deceiving since it plays a very important and complex role in biological systems (Grant 1978). High-precision measurements of the complex permittivity are expected to assist in providing a deeper understanding of the structure of water and its interactions in complex systems. The history of these measurements has been summarized by Zaghoul and Buckmaster (1985) who attained a 1σ precision of $\sim 0.06\%$. More recent measurements have been reported by van Kalleveen and Buckmaster (1988), Buckmaster *et al* (1989) and Steinhoff *et al* (1990). Kaatze (1989) summarized all results in the literature. Recent improvements in the microwave complex permittivity spectrometer first described by McAvoy and Buckmaster (1983) have enabled the data given in this paper to attain a 1σ precision of $\sim 0.03\%$.

The complex permittivity is a function of the temperature and pressure of the liquid and the measurement frequency. Most complex permittivity measurements have been made as function of frequency at a constant temperature and pressure. This paper reports comprehensive 9.355 GHz measurements on double-distilled, deionized water from 1 °C to 90 °C in ~ 2 °C steps. Although the literature reports measurements on water over various temperature intervals, most involve 5 °C temperature steps and none has reported above 75 °C (Mason *et al* 1974, Kaatze and Uhlendorf 1981,

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Kaatze 1989). This paper reports the first measurements of the complex permittivity of water above 75 °C. The measurements reported in this paper have been used to calculate empirical polynomial expressions for the temperature (T) dependence of the permittivity (ϵ') and the dielectric loss (ϵ''). Non-linear fitting of this data over 8 °C temperature intervals to the Cole–Cole equations (Cole and Cole 1948) enabled the temperature dependence of the dielectric relaxation time (τ) and the thermodynamic parameters, the free energy of activation (ΔF), the entropy of activation (ΔS) and the enthalpy of activation (ΔH) to be calculated from fixed frequency data for the first time. This method of data analysis has yielded the first report of the temperature dependence of the thermodynamic parameters for water using the temperature dependence of the complex permittivity. Previous analyses of water by Mason *et al* (1974), Zaghoul and Buckmaster (1985) and Steinhoff *et al* (1990) assumed that ΔF , ΔS and ΔH were temperature independent over temperature intervals of ~ 30 °C. A comparison is also made between the values of these parameters obtained in this paper at various temperatures and those given in the literature.

2. Theory

The complex permittivity ϵ^* is given by

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1)$$

The spectrometer used utilizes a microwave transmission sample cell. Consequently, the attenuation coefficient α and phase shift coefficient β are related to the permittivity ϵ' and dielectric loss ϵ'' by

$$\epsilon' = (\lambda/\lambda_c)^2 + (\lambda/2\pi)^2(\beta^2 - \alpha^2) \quad (2a)$$

$$\epsilon'' = (\lambda/2\pi)^2 2\alpha\beta \quad (2b)$$

where λ is the free-space wavelength and λ_c is the cut-off wavelength of the waveguide (Jordan and Balmain 1968).

The first theoretical equations for the complex permittivity of dielectrics were derived by Debye (1929). Later Cole and Cole (1941) showed that an improved fit with experimental data was obtained by introducing a frequency-independent empirical parameter α (not the attenuation coefficient) to the Debye equations:

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/[1 + (i\omega\tau)^{(1-\alpha)}] \quad (3a)$$

$$\epsilon'(\omega) = (\epsilon_0 - \epsilon_\infty)[1 + (\omega\tau)^{(1-\alpha)} \sin(\alpha\pi/2)]/[1 + 2(\omega\tau)^{(1-\alpha)} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}] + \epsilon_\infty \quad (3b)$$

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty)(\omega\tau)^{(1-\alpha)} \cos(\alpha\pi/2)/[1 + 2(\omega\tau)^{(1-\alpha)} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}] \quad (3c)$$

where ϵ_0 is the static (zero-frequency) permittivity, ϵ_∞ is the 'infinite-frequency' permittivity, ω is the angular frequency and τ is the dielectric relaxation time. The

parameters in equations (3b) and (3c) must be expressed in terms of the temperature T to obtain the temperature dependence for ϵ' and ϵ'' .

Table 1 of Mason *et al* (1974) can be used to show that $\alpha = 0.013(2)$ and $\epsilon_\infty = 4.25(15)$ over the temperature interval 0°C to 75°C. However, Kaatze (1989) has reported that recent measurements of ϵ' and ϵ'' are consistent with $\alpha = 0.000$ and

$$\epsilon_\infty = 5.77 - 2.74 \times 10^{-2}T \quad (4)$$

where T is in °C. His data are also consistent with $\alpha = 0.000$ and $\epsilon_\infty = 5.54(32)$ between -4.1°C and 35°C.

The temperature dependence of $\epsilon_0(T)$ has been fitted to an exponential function by Malmberg and Maryott (1956) and Vidulich *et al* (1967). Zaghoul and Buckmaster (1985) and Steinhoff *et al* (1990) used the values reported by the latter.

$$\epsilon_0(T) = \epsilon_0(0) \exp(bT) \quad (5)$$

where $\epsilon_0(0) = 87.9103$, $b = -0.00458$ (°C⁻¹) and T is in °C.

The dielectric relaxation time τ was modelled using the expression derived by Eyring from the theory of absolute reaction rates (Conway 1959, Grant *et al* 1978, Zaghoul and Buckmaster 1985 and Steinhoff *et al* 1990):

$$\tau = [h/k(T + 273.15)] \exp[\Delta H/R(T + 273.15)] \exp(-\Delta S/R) \quad (6)$$

where h is Planck's constant k is Boltzmann's constant, and R is the gas constant. τ can be calculated using equation (6) if the value of ΔS and ΔH are known, and ΔF can also be calculated since $\Delta F = \Delta H - (T + 273.15)\Delta S$.

3. Instrumentation

The spectrometer is a semi-automated, dual-channel, double-superheterodyne, quasi-synchronous demodulation, variable-length transmission sample cell system. A detailed description of the current version of this spectrometer and its improvements as well as the methodology used to obtain the complex permittivity data reported in this paper has been given by Buckmaster *et al* (1990) and Buckmaster (1990, 1991). A data set consisted of twenty measurement sequences at each temperature after the sample water temperature had attained equilibrium. Each measurement sequence comprised two hundred data point pairs consisting of amplitude and phase measurements after the transmission cell length had been incremented by 31.75 μm (0.00125"). The measurements were made in the sample length region where the effects of reflections and modal resonances are negligible, so that the values of the incremental attenuation are independent of the sample cell length to within $\approx 0.06\%$. Extreme care was also taken to ensure that the temperature stability and homogeneity of the sample was $\sim \pm 0.01^\circ\text{C}$. This was achieved by (i) using sample cell cooling/heating jackets, (ii) surrounding the sample cell with cotton batting as insulation and (iii) doing three preliminary runs (without data acquisition) prior to the twenty data acquisition runs at each temperature. These steps as well as the many improvements outlined by Buckmaster *et al* (1990) and Buckmaster (1990, 1991), have enabled the spectrometer to produce measurements with a typical 1σ precision

of $\sim 0.03\%$. The most important of these other improvements was the use of a stepping motor to increment the sample cell length and to operate the spectrometer under computer control. The 1σ accuracy of $\sim 0.1\%$ has been estimated from measurements designed to test the effect of various changes to the instrumentation system and the $\pm 0.01^\circ\text{C}$ estimated temperature stability and homogeneity of the sample cell.

4. Results

The empirical polynomial expressions were calculated and the non-linear fit of the data to the Cole-Cole equations was performed after the data acquisition had been completed using fitting techniques given by Press *et al* (1988). Table 1 lists the values of the attenuation and phase shift coefficients obtained at different temperatures as well as the permittivity and the dielectric loss. Figure 1 is a graph of the temperature variation of the permittivity and dielectric loss. A linear fit to these data resulted in the following empirical polynomial equations:

$$\begin{aligned} \epsilon'(T) = & 43.789(18) + 1.4098(18)T - 3.008(26) \times 10^{-2}T^2 + 2.249(71) \times 10^{-4}T^3 \\ & - 2.33(85) \times 10^{-7}T^4 - 3.14(36) \times 10^{-9}T^5 \end{aligned} \quad (7a)$$

$$\begin{aligned} \epsilon''(T) = & 39.9615(91) - 1.77(20) \times 10^{-2}T - 3.350(13) \times 10^{-2}T^2 + 8.387(36) \times 10^{-4}T^3 \\ & - 8.470(42) \times 10^{-6}T^4 + 3.146(18) \times 10^{-8}T^5. \end{aligned} \quad (7b)$$

A comparison with similar polynomial equations given by Zaghoul and Buckmaster (1985), van Kalleveen and Buckmaster (1988) and Buckmaster *et al* (1989) shows that the improved precision as well as the larger temperature interval results in coefficients with smaller standard deviations.

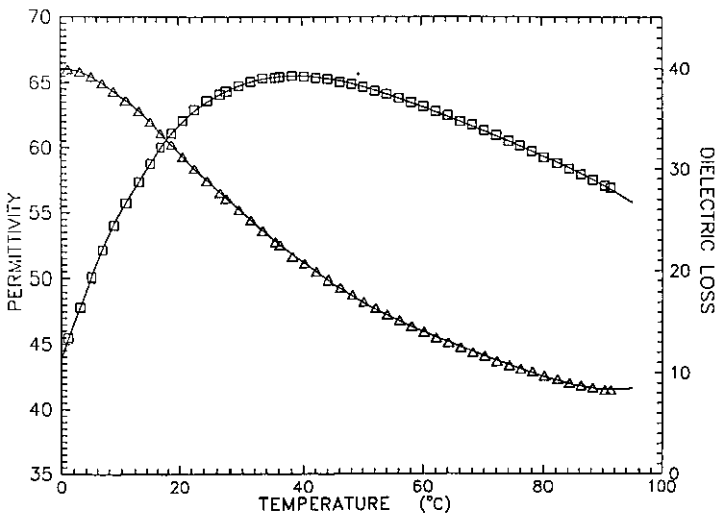


Figure 1. Graph showing the temperature dependence of the permittivity ϵ' (left ordinate) (\square), the dielectric loss ϵ'' (right ordinate) (Δ) and the linear fitted empirical curves (solid lines) for double-distilled, deionized water at 9.355 GHz.

Table 1. Table giving the attenuation coefficient α , phase shift coefficient β , permittivity ϵ' and dielectric loss ϵ'' and their standard deviations for double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to \sim 90 °C.

T (°C)	α (Np m ⁻¹)	β (rad m ⁻¹)	ϵ'	ϵ''
1.13	538.658(92)	1422.485(180)	45.471(13)	39.864(9)
3.07	525.406(79)	1448.630(182)	47.791(15)	39.598(7)
4.99	510.690(73)	1473.395(187)	50.070(16)	39.147(7)
6.96	494.946(86)	1494.970(178)	52.148(15)	38.496(8)
8.91	478.694(64)	1513.893(170)	54.040(14)	37.703(6)
10.84	462.178(69)	1530.388(189)	55.751(16)	36.799(6)
12.82	445.086(93)	1545.438(182)	57.358(15)	35.786(9)
14.78	428.346(84)	1558.045(197)	58.757(17)	34.721(7)
16.75	411.318(58)	1569.291(188)	60.043(14)	33.582(8)
18.73	395.414(60)	1578.349(175)	61.119(15)	32.470(5)
20.71	379.003(77)	1586.214(203)	62.097(16)	31.277(6)
22.71	362.946(86)	1592.572(210)	62.933(19)	30.072(9)
24.69	347.234(57)	1597.429(186)	63.626(14)	28.858(6)
26.67	332.479(71)	1600.060(183)	64.106(15)	27.677(7)
27.61	325.482(67)	1601.465(144)	64.342(10)	27.119(7)
29.59	311.506(54)	1603.605(156)	64.752(13)	25.989(6)
31.57	299.241(64)	1605.209(175)	65.081(15)	24.991(5)
33.55	286.422(77)	1606.047(200)	65.346(17)	23.932(8)
35.57	273.733(70)	1604.256(179)	65.382(15)	22.847(7)
36.29	270.400(75)	1604.372(126)	65.439(10)	22.570(7)
38.31	259.572(59)	1603.116(172)	65.523(14)	21.399(5)
40.31	248.799(70)	1601.134(168)	65.460(14)	20.725(6)
42.30	239.504(65)	1598.673(149)	65.374(12)	19.920(6)
44.27	230.674(72)	1596.418(154)	65.294(13)	19.159(6)
46.27	222.482(78)	1592.443(150)	65.061(12)	18.432(7)
48.26	214.437(77)	1589.361(178)	64.897(15)	17.731(7)
50.29	206.733(51)	1585.681(130)	64.678(10)	17.055(4)
52.31	199.583(50)	1581.031(133)	64.379(11)	16.417(4)
54.26	192.242(90)	1577.292(206)	64.138(17)	15.775(8)
56.26	185.696(57)	1572.725(185)	63.828(15)	15.194(5)
58.24	179.377(54)	1568.199(150)	63.518(12)	14.635(4)
60.25	172.692(48)	1563.484(149)	63.195(12)	14.047(4)
62.25	166.540(63)	1558.267(164)	62.826(13)	13.502(5)
64.24	160.729(69)	1553.763(187)	62.511(15)	12.993(6)
66.22	155.460(72)	1547.435(202)	62.044(16)	12.516(6)
68.23	149.864(54)	1543.579(151)	61.778(12)	12.035(4)
70.21	145.758(62)	1537.710(189)	61.339(15)	11.661(5)
72.25	139.827(46)	1532.391(165)	60.959(13)	11.148(4)
74.30	135.190(74)	1526.112(162)	60.492(13)	10.734(6)
76.20	131.407(88)	1521.278(205)	60.135(16)	10.400(7)
78.21	128.514(65)	1515.547(191)	59.702(15)	10.133(5)
80.25	123.959(63)	1509.236(189)	59.235(15)	9.733(5)
82.30	120.048(52)	1503.177(180)	58.785(14)	9.388(4)
84.30	116.113(42)	1497.461(147)	58.363(11)	9.046(3)
86.31	113.287(43)	1491.519(142)	57.918(11)	8.791(3)
88.27	110.901(52)	1486.031(169)	57.507(13)	8.574(4)
90.31	108.628(93)	1480.195(210)	57.070(16)	8.365(7)
91.33	108.292(100)	1478.046(250)	56.906(19)	8.327(8)

The temperature dependences of ΔS and ΔH were determined by assuming that these parameters were constant over a small temperature interval of \sim 8 °C. A

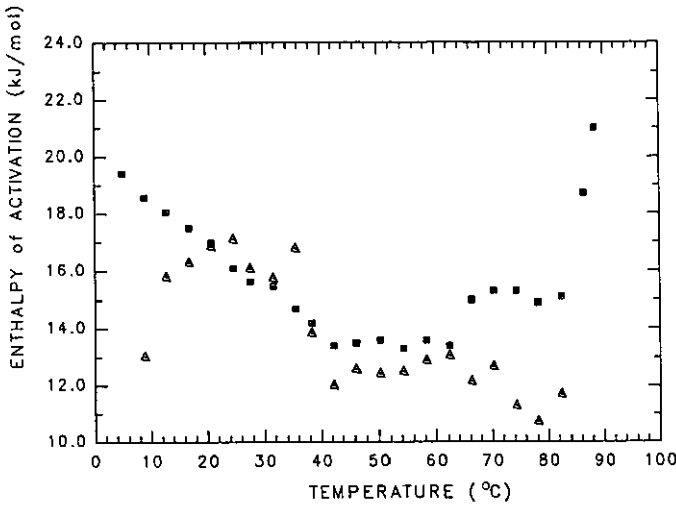


Figure 2. Graph showing the temperature dependence of the enthalpy of activation ΔH for double-distilled, deionized water at 9.355 GHz. The data points are from table 2 for $\Delta H_{\epsilon'}$ (\square) and for $\Delta H_{\epsilon''}$ (Δ) using the Kaatze (1989) values for α and ϵ_{∞} .

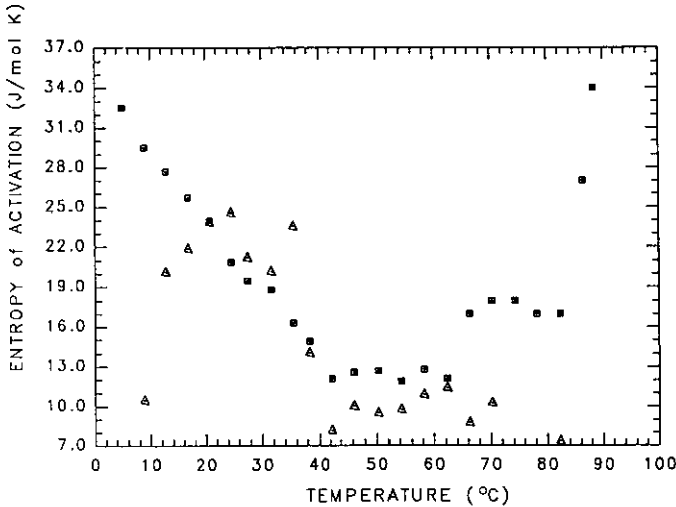


Figure 3. Graph showing the temperature dependence of the entropy of activation ΔS for double-distilled, deionized water at 9.355 GHz. The data points are from table 3 for $\Delta S_{\epsilon'}$ (\square) and for $\Delta S_{\epsilon''}$ (Δ) using the Kaatze (1989) values for α and ϵ_{∞} .

non-linear fit was performed on intervals consisting of five data temperatures starting at the lowest temperature (1.13°C). Each interval consisted of three temperatures from the previous interval (e.g. the first interval had 1.13, 3.07, 4.99, 6.96, 8.91°C, the second interval had 4.99, 6.96, 8.91, 10.84, 12.82°C, etc.). The values obtained for ΔS and ΔH were then attributed to the central temperature of each interval (e.g. the central temperature for the first interval was 4.99°C). A non-linear fit of equations (3b) and (3c) to the ϵ' and ϵ'' data sets provides the temperature variation of the enthalpy of activation $\Delta H(T)$ and entropy of activation $\Delta S(T)$. These fits have been performed using the values of α and ϵ_{∞} given by both Mason *et al* (1974) and Kaatze (1989). The fitting of equation (3b) gives the values of $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$, and equation (3c) gives $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$. The temperature dependences of the thermodynamic parameters ΔH and ΔS , calculated using $\alpha = 0.000$ and ϵ_{∞} from equation (4), are given in figures 2 and 3 respectively. The values of these parameters are given in tables 2 and 3 for both pairs of α and ϵ_{∞} values. The values

reported in the literature for ΔH and ΔS , obtained assuming that these parameters were temperature independent, are listed below tables 2 and 3. These values are consistent with those reported in this paper.

Table 2. Table of values for the enthalpy of activation ΔH and their standard deviations for double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to 90 °C; values of ΔH were obtained by fitting the expressions for the permittivity ϵ' and dielectric loss ϵ'' using the Mason *et al* (1974) and Kaatze (1989) values for α and ϵ_∞ .

T (°C)	Mason <i>et al</i> (1974) $\alpha = 0.013$ and $\epsilon_\infty = 4.25$		Kaatze (1989) $\alpha = 0$ and ϵ_∞ (equation (4))	
	$\Delta H_{\epsilon'}$ kJ mol ⁻¹	$\Delta H_{\epsilon''}$ kJ mol ⁻¹	$\Delta H_{\epsilon'}$ kJ mol ⁻¹	$\Delta H_{\epsilon''}$ kJ mol ⁻¹
4.99	19.69(38)	6.037(91)	19.42(37)	6.058(83)
8.91	18.92(46)	13.542(84)	18.56(45)	13.027(78)
12.82	18.48(48)	16.258(60)	18.06(47)	15.767(54)
16.75	17.95(59)	16.712(55)	17.49(57)	16.280(52)
20.71	17.49(64)	17.237(47)	16.99(62)	16.851(45)
24.69	16.59(76)	17.429(51)	16.08(74)	17.077(49)
27.61	16.2(1.0)	16.326(46)	15.64(97)	16.060(45)
31.57	16.00(90)	15.964(50)	15.45(87)	15.738(49)
35.57	15.2(1.4)	17.000(47)	14.7(1.3)	16.771(46)
38.31	14.8(1.3)	13.940(58)	14.2(1.3)	13.836(56)
42.30	13.9(1.4)	12.032(50)	13.4(1.4)	12.001(48)
46.27	14.1(1.5)	12.578(46)	13.5(1.4)	12.561(45)
50.29	14.2(2.0)	12.389(64)	13.6(1.9)	12.400(63)
54.26	13.9(2.1)	12.444(44)	13.3(2.0)	12.484(42)
58.24	14.3(3.1)	12.809(66)	13.6(2.9)	12.870(62)
62.25	14.1(3.5)	12.960(63)	13.4(3.3)	13.043(61)
66.22	15.9(4.1)	12.012(67)	15.0(3.9)	12.151(66)
70.21	16.2(5.0)	12.490(79)	15.3(4.7)	12.651(77)
74.30	16.2(6.5)	11.033(83)	15.3(6.0)	11.261(80)
78.21	15.9(7.0)	10.447(90)	14.9(6.6)	10.724(88)
82.30	16.2(7.7)	11.383(75)	15.1(7.2)	11.674(73)
86.31	20(11)	8.248(97)	18.7(9.7)	8.636(94)
88.27	23(13)	6.06(11)	21(11)	6.51(11)

Conway (1959): 19.51(30) kJ mol⁻¹ (0 °C to 34 °C).

Conway (1959): 13.79(20) kJ mol⁻¹ (30 °C to 77 °C).

Kaatze and Uhlendorf (1981): 20.50(40) kJ mol⁻¹ (-5 °C to 60 °C).

Zaghloul and Buckmaster (1985): 16.30(1) kJ mol⁻¹ (10 °C to 40 °C).

Steinhoff *et al* (1990): 16.45(12) kJ mol⁻¹ (6 °C to 45 °C).

The values of ΔH and ΔS calculated from the fits of equations (3b) and (3c) using the ϵ' and ϵ'' data sets given in tables 2 and 3 respectively are consistent from ~ 20 °C to ~ 80 °C within the $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$, 1σ errors but not within the $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$, 1σ errors, because the 1σ errors for $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$ are at least an order of magnitude smaller than those for $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$. The value of $\alpha \ll \beta$ so the accuracy of ϵ' is determined primarily by β because $\epsilon' \propto \beta^2 - \alpha^2$ whereas the accuracy of ϵ'' is determined primarily by α because $\epsilon'' \propto \alpha\beta$. Consequently, the values of $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$ are more reliable than $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$. If it is assumed that $\Delta H_{\epsilon'}(T) = \Delta H_{\epsilon''}(T)$, then it can be estimated that $\alpha(1.13) \approx 560$ Np m⁻¹ rather than 538.66 Np m⁻¹ given in table 1. This implies that the recorded sample cell temperature is lower than the actual sample temperature

Table 3. Table of values for the entropy of activation ΔS and their standard deviations for double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to 90 °C; values of ΔS were obtained from non-linear fitting of the expressions for the permittivity ϵ' and dielectric loss ϵ'' using the Mason *et al* (1974) and Kaatze (1989) values for α and ϵ_∞ .

T (°C)	Mason <i>et al</i> (1974) $\alpha = 0.013$ and $\epsilon_\infty = 4.25$		Kaatze (1989) $\alpha = 0$ and ϵ_∞ (equation (4))	
	$\Delta S_{\epsilon'}$ (J mol ⁻¹ K ⁻¹)	$\Delta S_{\epsilon''}$ (J mol ⁻¹ K ⁻¹)	$\Delta S_{\epsilon'}$ (J mol ⁻¹ K ⁻¹)	$\Delta S_{\epsilon''}$ (J mol ⁻¹ K ⁻¹)
4.99	33.6(1.4)	-14.52(32)	32.5(1.3)	-14.37(30)
8.91	30.9(1.6)	12.21(30)	29.5(1.6)	10.45(28)
12.82	29.4(1.7)	21.77(21)	27.7(1.6)	20.10(19)
16.75	27.5(2.0)	23.34(19)	25.7(2.0)	21.87(18)
20.71	25.9(2.2)	25.14(16)	24.0(2.1)	23.83(15)
24.69	22.9(2.6)	25.79(17)	20.9(2.5)	24.59(16)
27.61	21.5(3.4)	22.11(15)	19.5(3.2)	21.20(15)
31.57	20.9(3.0)	20.92(16)	18.8(2.9)	20.14(16)
35.57	18.4(4.4)	24.29(15)	16.3(4.2)	23.51(15)
38.31	17.1(4.3)	14.41(18)	14.9(4.1)	14.02(18)
42.30	14.2(4.5)	8.34(16)	12.1(4.3)	8.19(15)
46.27	14.8(4.6)	10.06(14)	12.6(4.4)	9.96(14)
50.29	15.1(6.2)	9.48(20)	12.7(5.9)	9.46(19)
54.26	14.3(6.5)	9.64(13)	11.9(6.1)	9.71(13)
58.24	15.4(9.4)	10.76(20)	12.8(8.9)	10.89(19)
62.25	15(11)	11.20(19)	12.1(9.9)	11.41(18)
66.22	20(12)	8.40(20)	17(12)	8.76(19)
70.21	21(15)	9.80(23)	18(14)	10.23(23)
74.30	21(19)	5.57(23)	18(17)	6.19(23)
78.21	20(20)	3.91(25)	17(19)	4.67(25)
82.30	21(22)	6.55(21)	17(20)	7.35(21)
86.31	32(29)	-2.22(27)	27(27)	-1.14(26)
88.27	40(35)	-8.32(32)	34(32)	-7.06(31)

Conway (1959): 33.34(1.9) J mol⁻¹ K⁻¹ (0 °C to 34 °C).

Conway (1959): 14.00(85) J mol⁻¹ K⁻¹ (30 °C to 77 °C).

Zaghloul and Buckmaster (1985): 22.26(2) J mol⁻¹ K⁻¹ (10 °C to 40 °C).

Steinhoff *et al* (1990): 22.62(1.0) J mol⁻¹ K⁻¹ (6 °C to 45 °C).

as α increases as the temperature decreases. This temperature difference probably occurs because a gradient exists. The same conclusion is obtained if it is assumed that $\Delta S_{\epsilon'}(T) = \Delta S_{\epsilon''}(T)$. At temperatures above 75 °C, water develops microbubbles of water vapour which increase in diameter as the temperature approaches the boiling point (~ 95 °C at ~ 1 km). Consequently, the measured values of β are lower than the theoretical values and the values of $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$ are more reliable than $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$, although the percentage error for both α and β increases as the temperature increases. It is also possible that some of the divergence in the values of $\Delta H_{\epsilon'}$ and $\Delta H_{\epsilon''}$, as well as $\Delta S_{\epsilon'}$ and $\Delta S_{\epsilon''}$, is due to sample cell thermal inhomogeneity. It is concluded that the temperature variation of both ΔH and ΔS follows the values of $\Delta H_{\epsilon'}$ and $\Delta S_{\epsilon'}$, respectively up to ~ 60 °C. Above ~ 60 °C, it is concluded that the more reliable values are those for $\Delta H_{\epsilon''}$ and $\Delta S_{\epsilon''}$.

Neutron scattering (Ohtomo *et al* 1982) indicates that the primary structure of liquid water from ~ 20 °C to ~ 90 °C is a mixture of tetrahedral pentamers and non-bonded monomers. The value of the permittivity ϵ' is an indicator of the ease with

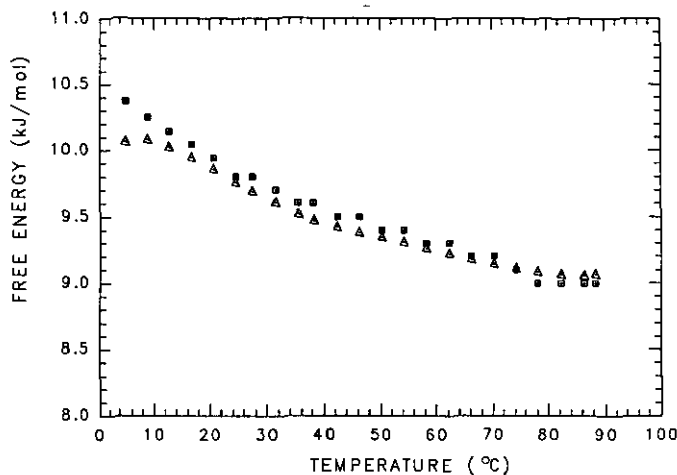


Figure 4. Graph showing the temperature dependence of the free energy of activation ΔF for double-distilled deionized water at 9.355 GHz. The data points are from table 4 for $\Delta F_{e'}$ (\square) and for $\Delta F_{e''}$ (Δ) using the Kaatze (1989) values for α and ϵ_{∞} .

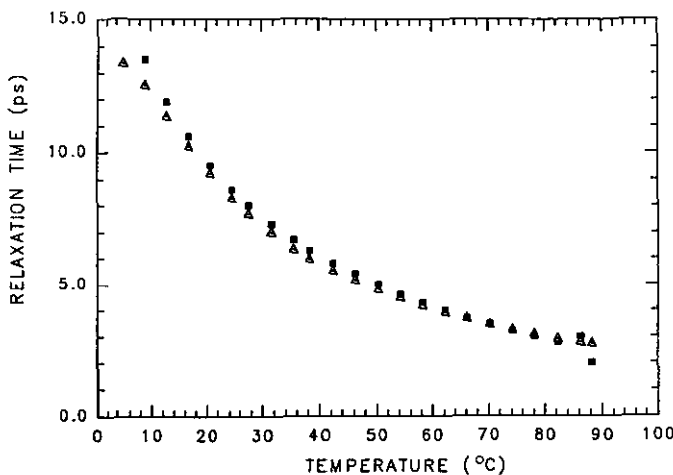


Figure 5. Graph showing the temperature dependence of the dielectric relaxation time τ for double-distilled, deionized water at 9.355 GHz. The data points are from table 5 for $\tau_{e'}$ (\square) and for $\tau_{e''}$ (Δ) using the Kaatze (1989) values for α and ϵ_{∞} .

which the molecular dipoles can follow changes in the direction of the electric field (Grant *et al* 1978). The lower the permittivity value the less able the molecular dipoles are to follow the changes in the electric field. The maximum value of the permittivity occurs at a temperature which is near the change in slope of the temperature dependence of the entropy and enthalpy of activation. This indicates that the molecular environment of the water has reached a state which permits the dipolar molecules to follow the electric field changes most easily at the measurement frequency of 9.355 GHz, which may be because the ratio of tetrahedral pentamers to non-bonded monomers is less than a critical value.

Tables 2 and 3 also reveal that the values of ΔH and ΔS are insensitive to the values of α and ϵ_{∞} used except above $\sim 70^{\circ}\text{C}$. It is noted that the values of ΔH and ΔS calculated using $\alpha = 0.013(2)$ of Mason *et al* (1974) and $\epsilon_{\infty} = 5.54(32)$ of Kaatze (1989) also agree within 1σ with the values of ΔH and ΔS given in tables 2 and 3. Trial calculations on intervals consisting of four and six rather than five successive data temperatures yielded essentially the same values of ΔH and ΔS within 1σ .

Table 4. Table of values for the free energy of activation ΔF and their standard deviations for double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to 90 °C; the values of ΔF were obtained from the values of ΔH and ΔS given in tables 2 and 3 respectively using $\Delta F = \Delta H - (T + 273.15)\Delta S$.

T (°C)	Mason <i>et al</i> (1974) $\alpha = 0.013$ and $\epsilon_\infty = 4.25$		Kaatz (1989) $\alpha = 0$ and ϵ_∞ (equation (4))	
	$\Delta F_{\epsilon'}$ (kJ mol ⁻¹)	$\Delta F_{\epsilon''}$ (kJ mol ⁻¹)	$\Delta F_{\epsilon'}$ (kJ mol ⁻¹)	$\Delta F_{\epsilon''}$ (kJ mol ⁻¹)
4.99	10.33(53)	10.08(13)	10.37(52)	10.06(12)
8.91	10.20(65)	10.10(12)	10.25(64)	10.08(11)
12.82	10.08(68)	10.031(85)	10.14(66)	10.018(76)
16.75	9.97(83)	9.945(77)	10.04(81)	9.938(74)
20.71	9.87(91)	9.849(66)	9.94(88)	9.848(63)
24.69	9.8(1.1)	9.748(72)	9.8(1.0)	9.752(69)
27.61	9.7(1.4)	9.678(65)	9.8(1.4)	9.685(63)
31.57	9.6(1.3)	9.590(71)	9.7(1.2)	9.600(69)
35.57	9.5(1.9)	9.501(67)	9.6(1.8)	9.514(65)
38.31	9.5(1.9)	9.452(81)	9.6(1.8)	9.467(79)
42.30	9.4(2.0)	9.401(70)	9.5(1.9)	9.417(68)
46.27	9.4(2.0)	9.364(65)	9.5(2.0)	9.380(63)
50.29	9.3(3.0)	9.324(91)	9.4(2.7)	9.341(89)
54.26	9.3(3.0)	9.286(62)	9.4(2.8)	9.303(60)
58.24	9.2(4.4)	9.245(93)	9.3(4.1)	9.261(89)
62.25	9.1(5.0)	9.202(89)	9.3(4.7)	9.217(87)
66.22	9.1(5.9)	9.163(95)	9.2(5.5)	9.177(93)
70.21	9.0(7.1)	9.12(11)	9.2(6.6)	9.14(11)
74.30	8.9(9.2)	9.10(12)	9.1(8.5)	9.11(11)
78.21	9(10)	9.07(13)	9.0(9.4)	9.08(12)
82.30	9(11)	9.06(11)	9(10)	9.06(10)
86.31	9(15)	9.05(14)	9(13)	9.05(13)
88.27	9(18)	9.06(16)	9(16)	9.06(15)

The values for $\Delta H(T)$ and $\Delta S(T)$ were used to calculate the values of $\Delta F(T)$ and of $\tau(T)$ which are given in tables 4 and 5 respectively. These values are also insensitive to the values of α and ϵ_∞ used. Figures 4 and 5 are graphs of ΔF and τ respectively as functions of the temperature.

The values of ΔF and τ , obtained using the ϵ' and ϵ'' data sets, are consistent to within the 1σ error over the interval 1 °C to 90 °C, and the 1σ errors for $\Delta F_{\epsilon''}$ and $\tau_{\epsilon''}$ are also at least an order of magnitude smaller than those for $\Delta F_{\epsilon'}$ and $\tau_{\epsilon'}$. Table 5 also includes those values of τ given by Mason *et al* (1974) and Kaatz (1989). There is excellent agreement between these four data sets in the temperature interval where they overlap. The values of ΔF and τ calculated from the ϵ' and ϵ'' data sets also diverge above ~ 60 °C but the differences are much smaller than for ΔH and ΔS and the values do not scatter. It is probable that these divergences are also due to the fact that the sample thermal homogeneity degrades with increasing temperature. Nevertheless, the temperature dependence of the thermodynamic parameters and the relaxation time have been determined reasonably reliably from 10 °C to 60 °C and less reliably below 10 °C and above 60 °C. Further work is continuing to improve the precision and accuracy of the instrumentation used to make these measurements. It is suggested that calculations of the temperature dependence of ΔH and ΔS using the temperature dependence of ϵ' and ϵ'' can be used as a diagnostic test for

Table 5. Table of values of the relaxation time τ and its standard deviations for double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to 90 °C; the values of τ were obtained by using the values of ΔH and ΔS given in tables 2 and 3, and equation (4).

T (°C)	Mason <i>et al</i> (1974) $\alpha = 0.013$ $\epsilon_{\infty} = 4.25$		Kaatze (1989) $\alpha = 0$ ϵ_{∞} (equation (4))		Mason <i>et al</i> (1974)	Kaatze (1989)
	$\tau_{e'}$ (ps)	$\tau_{e''}$ (ps)	$\tau_{e'}$ (ps)	$\tau_{e''}$ (ps)	τ (ps)	τ (ps)
0	—	—	—	—	17.90(60)	17.61
4.99	15.0(3.5)	13.47(74)	15.3(3.4)	13.34(68)	—	14.90
8.91	13.2(3.7)	12.61(64)	13.5(3.7)	12.51(59)	—	13.14
10	—	—	—	—	12.61(29)	12.70
12.82	11.7(3.3)	11.41(41)	11.9(3.3)	11.34(36)	—	11.65
16.75	10.4(3.6)	10.25(33)	10.6(3.6)	10.22(31)	—	10.38
20	—	—	—	—	9.31(08)	9.47
20.71	9.3(3.4)	9.20(25)	9.5(3.4)	9.19(24)	—	9.28
24.69	8.3(3.6)	8.25(24)	8.6(3.6)	8.27(23)	—	8.34
27.61	7.7(4.4)	7.65(20)	8.0(4.4)	7.67(19)	—	7.73
30	—	—	—	—	7.21(10)	7.29
31.57	7.0(3.5)	6.94(19)	7.3(3.5)	6.96(19)	—	7.01
35.57	6.4(4.8)	6.30(17)	6.7(4.8)	6.33(16)	—	6.38
38.31	6.0(4.4)	5.93(19)	6.3(4.4)	5.96(18)	—	5.99
40	—	—	—	—	5.83(09)	5.78
42.30	5.5(4.3)	5.48(15)	5.8(4.3)	5.52(14)	—	5.50
46.27	5.1(4.0)	5.11(13)	5.4(4.0)	5.14(12)	—	5.07
50	—	—	—	—	4.76(09)	4.72
50.29	4.7(5.0)	4.76(16)	5.0(5.0)	4.79(16)	—	4.69
54.26	4.4(4.8)	4.44(10)	4.6(4.8)	4.47(10)	—	4.36
58.24	4.1(6.5)	4.15(14)	4.3(6.5)	4.17(14)	—	4.07
60	—	—	—	—	3.95(13)	3.95
62.25	3.8(6.9)	3.88(12)	4.0(6.8)	3.90(12)	—	3.81
66.22	3.5(7.3)	3.64(12)	3.7(7.3)	3.66(12)	—	3.59
70.21	3.2(8.1)	3.41(13)	3.5(8.1)	3.43(13)	—	3.38
74.30	3.0(9.5)	3.22(13)	3.2(9.5)	3.23(13)	—	3.20
75	—	—	—	—	3.20(17)	3.17
78.21	2.8(9.6)	3.05(13)	3.0(9.7)	3.06(13)	—	3.04
82.30	2.6(9.6)	2.89(10)	2.8(9.6)	2.90(10)	—	2.89
86.31	2(12)	2.75(13)	3(12)	2.76(12)	—	2.76
88.27	2(13)	2.71(15)	2(13)	2.71(14)	—	2.70

the evaluation of the existence of errors and inconsistencies in complex permittivity data sets. These inconsistencies may arise because of deficiencies in the design of the variable-length sample cell system. It is suggested that the lower, fixed waveguide section of the cell requires additional thermal mass to improve the sample thermal homogeneity particularly at measurements below ~ 10 °C and that additional thermal insulation of the entire sample cell system will improve this homogeneity and stability above ~ 60 °C.

5. Summary

This paper has reported the first determination of the complex permittivity of double-distilled, deionized water at 9.355 GHz in the temperature interval 1 °C to 90 °C

in $\sim 2^\circ\text{C}$ steps. The temperature dependence of τ for water in this temperature interval is given and compared with the values given by Mason *et al* (1974) and Kaatze (1989). It also reports the first determination of the temperature dependence of the thermodynamic parameters ΔH , ΔS and ΔF for water in this temperature interval. This dependence is consistent with a model of water consisting primarily of tetrahedral pentamers below $\sim 40^\circ\text{C}$ and primarily non-bonded monomers above $\sim 40^\circ\text{C}$. It has been shown that the temperature dependence of the calculated values of these parameters for water is insensitive to the choice of various pairs of α and ϵ_∞ values reported in the literature to within 1σ . It has been demonstrated that the consistency in the calculation of the pairs $\Delta S_{\epsilon'}$ and $\Delta S_{\epsilon''}$, and $\Delta H_{\epsilon'}$ and $\Delta H_{\epsilon''}$ can be used as a diagnostic test to improve the design of the instrumentation used to make complex permittivity measurements.

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