The relative permittivity of supercooled water

I. M. Hodge and C. A. Angell

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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Approximate relative permittivity data for water down to -35°C have been derived from measurements of the Maxwell–Wagner interfacial polarization which occurs at the surface of emulsified water droplets. Although the emulsifying agent strongly influences this polarization in a complex way, a novel method of data analysis enables the permittivity and conductivity to be obtained in a simple and direct manner. The derived data are in essential agreement with literature data near 0°C. To within an estimated experimental uncertainty of $\pm 2\%$ the present data conform to a critical exponent expression with the same critical temperature (228 K) found for many other properties of supercooled water, though the divergence is very weak.

INTRODUCTION

Many of the physical properties of water in the supercooled liquid state exhibit strong temperature dependences which have been shown recently[1,2] to conform to the relation

$$P_i = P_i^0\,(T/T_s - 1)^{\gamma_i} \tag{1}$$

where P_i is the physical property, $T_s = 228$ K, and P_i^0 and γ_i are adjustable parameters. This equation describes within experimental scatter, the subzero temperature dependences of the isobaric heat capacity,[1] isothermal compressibility,[2] density,[3,4] diffusion coefficient,[5] bulk[6] and shear viscosity,[7] sound velocity and absorption,[6] proton spin–lattice relaxation time,[8] and oxygen spin–lattice relaxation time.[9] Equation (1) also describes the temperature dependence of the dielectric relaxation time in the range 0–+60 °C.[2,10] Conspicuous absences in this list are the two basic electrical properties of water, the static relative permittivity ϵ_0, and conductivity σ_0. In the present communication, approximate data on the temperature dependences of these quantities are reported, and their consistency with Eq. (1) is demonstrated.

Note added in proof: While print was being set, Dr. G. P. Johari drew our attention to a recent report by Hasted and Shahadi [Nature **262**, 777 (1976)] on the successful measurement of ϵ_0 to -35 °C using a technique with some elements in common with ours. Their method yielded results which agree with those reported below to well within the stated uncertainties of the two measuring techniques.

The chief difficulty encountered in studying supercooled water is, of course, that of preventing crystallization to ice I. This is most easily overcome by the use of small samples, which can be made by containing the water in fine glass capillaries, or by forming an emulsion of small water droplets in a hydrophobic medium (such as heptane) with the aid of an emulsifying agent. However, the determination of the electrical properties of such small samples is not straightforward. In this paper we report partial success in overcoming some of the difficulties, our approach being through the Maxwell–Wagner interfacial polarization phenomenon observed in emulsified water. To introduce this approach we review the fundamentals of the Maxwell–Wagner effect, and describe briefly the additional difficulties encountered in emulsified two-phase systems together with methods for overcoming them.

MAXWELL-WAGNER POLARIZATION

If a sphere of a conducting material is immersed in a nonconducting medium and an electric field is applied, polarization occurs at the interface which, upon removal of the field, relaxes with a single relaxation time determined primarily by the conductivity of the sphere. The magnitude of the polarization is determined by the relative permittivities of the sphere and the medium. If the sphere has specific conductivity σ_1 and relative permittivity ϵ_1, and the surrounding medium has a relative permittivity ϵ_2, the interfacial polarization relaxation time τ is given by[11,12]

$$\tau = \frac{(2\epsilon_1 + \epsilon_2)e_0}{\sigma_1}, \tag{2}$$

where e_0 is the permittivity of free space. At the frequency $f_{\max} = (2\pi\tau)^{-1}$, the dielectric loss passes through its maximum value $\epsilon''_{\max}$ given by[11,12]

$$\epsilon''_{\max} = \frac{9\gamma\epsilon_1^2}{2(2\epsilon_1 + \epsilon_2)}\left(1 + \frac{3\gamma(\epsilon_2 - \epsilon_1)}{(2\epsilon_1 + \epsilon_2)}\right), \tag{3}$$

where γ is the volume fraction of the sphere relative to the surrounding medium. Equations (2) and (3) are also valid for a collection of spheres, provided these do not interact with each other. It is clear that, in principle, determinations of $\epsilon''_{\max}$ and $f_{\max}$ enable ϵ_1 and σ_1 to be evaluated if ϵ_2 is known. For water emulsified in heptane, $2\epsilon_1 \gg \epsilon_2$ and these equations then simplify to

$$(2\pi f_{\max})^{-1} = \tau \approx \frac{2\epsilon_1 e_0}{\sigma_1}, \tag{4}$$

and

$$\epsilon''_{\max} \approx \frac{9\gamma\epsilon_1'}{4}\left(1 - \frac{3\gamma}{2}\right), \tag{5}$$

which are valid to within ca. 2%. However, a number of difficulties prevent access to the experimental conditions for which Eqs. (4) and (5) are appropriate. In the first place, the emulsions have a tendency to settle out at temperatures above 0 °C. To decrease the probability of this occurring, a mixture of heptane and carbon tetrachloride was used which had a density of 1 gm cm^{-3} at room temperature. The most effective method,

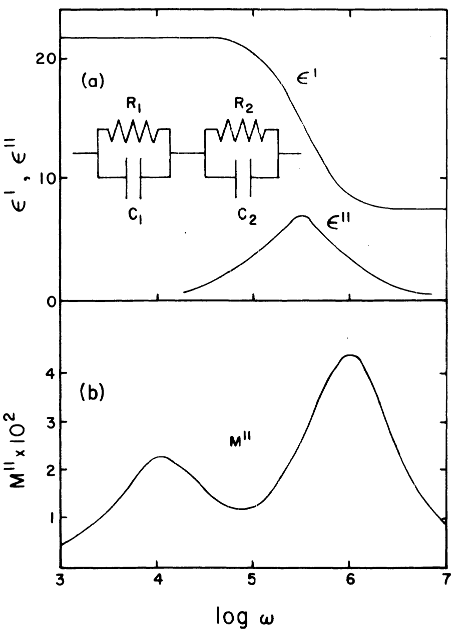

FIG. 1. (a) The frequency dependences of the relative permittivity ϵ' and relaxational part of the dielectric loss ϵ'' for the circuit shown. $R_1 = 5\times10^7$ Ω, $C_1 = 2\times10^{-12}$ F, $R_2 = 10^6$ Ω, and $C_2 = 10^{-12}$ F; (b) Frequency dependence of the electric loss modulus M'' for the circuit given in (a).

which proved to be essential, was to increase the viscosity of the emulsion by using a large volume fraction of water ($\gamma = 0.3$). At this concentration interactions between the droplets are probably strong, with resulting deviations from Eqs. (2) and (3). A second difficulty is contamination of the water by impurities in the emulsifying agent (sorbitan tristearate). This would probably significantly increase the conductivity of the water droplets, but would not be expected to alter the permittivity to any significant extent. By far the most serious problem, however, is generated by the emulsifying agent itself, since Eqs. (2)–(5) describe the polarization at the interface between the water and the nonconducting medium, and this interface includes the emulsifying agent.

The severity of the difficulties which ensue from this is exemplified by the observed decrease with decreasing temperature of ϵ_1' calculated from Eq. (5) (see Results). This absurd result indicates that the Maxwell–Wagner formula is not valid for these emulsions. The absurdity can be removed, however, by an appropriate method of data analysis. Such a method is described below, and its validity is demonstrated by the internal consistency of derived quantities and their agreement with short extrapolations of literature data taken at temperatures above 0 °C.

SIMULATION OF MAXWELL-WAGNER INTERFACIAL POLARIZATION

For the purposes of illustrating the basic nature of the difficulties encountered and the method used to circumvent them, the polarization between the water droplets and the emulsifier-containing interface with the nonconducting medium will be simulated by the electrical response of a circuit containing two parallel RC elements in series, as illustrated in Fig. 1(a). Such a simple circuit cannot be expected to duplicate exactly the electrical response of a system as complex as a water emulsion, of course, but it does simulate most of the essential features and therefore provides a convenient reference point for describing the advantages of the new method of data analysis. It also sheds some light on the origin of the inverted temperature dependence of ϵ_1 calculated from Eq. (5).

The primary features of the electrical response of the circuit are as follows. At angular frequencies lying between the two reciprocal Maxwell RC relaxation times, the element with the shorter relaxation time behaves as a pure resistance and the other acts as a pure capacitance. This series RC circuit gives a Debye peak when the dielectric loss ϵ'' is plotted against log frequency. At very low frequencies the circuit behaves as a pure resistance and therefore simulates a dc conductivity. The relaxation part of ϵ'', obtained by subtracting the conductivity loss from the total loss in the usual manner, is plotted against frequency in Fig. 1(a), together with the corresponding dispersion in relative permittivity ϵ'. The loss peak and the dispersion in ϵ' reflect the "interfacial polarization" between the two RC elements.

To simulate the Maxwell–Wagner conditions, R_2 must be very large compared with R_1. The maximum loss $\epsilon''_{\max}$ is then given by

$$\epsilon''_{\max} \sim \frac{1}{2}\,\frac{C_1C_2}{C_1+C_2} \sim \frac{k}{2}\,\frac{\epsilon_1\epsilon_2}{\epsilon_1+k\epsilon_2}\,, \qquad (6)$$

where the factor k is inserted to take into account the differences in geometry of the water droplet and the surrounding medium. If the latter is identified with the essentially monomolecular layer of emulsifier around each droplet the associated capacitance C_2 is very large (i.e., k is very large) and $\epsilon''_{\max} \sim \epsilon_1$, in agreement with Eq. (5).

The situation is complex, however, if the relaxation time of the thin monolayer is comparable with that of the water droplet. In this case $\epsilon''_{\max}$ is also determined by the conductivity of the water, which is much more strongly temperature dependent than ϵ_1. The expression for $\epsilon''_{\max}$ in this case is

$$\epsilon''_{\max} \sim \epsilon_0 \left(\frac{T-\epsilon_1/\sigma_1}{T+\epsilon_1/\sigma_1}\right)^2\,, \qquad (7)$$

where T is proportional to the relaxation time of the emulsifier monolayer, and ϵ_1/σ_1 similarly reflects the relaxation time of the water droplet. If the difference between these two relaxation times decreases with decreasing temperature more rapidly than ϵ_1 increases, a decrease in $\epsilon''_{\max}$ with decreasing temperature (such as that observed) results. An example of a physically reasonable situation in which this condition is met is that T be larger, but less temperature dependent than ϵ_1/σ_1. Although the temperature dependence of $\epsilon''_{\max}$ is unlikely to conform exactly to Eq. (7), the possibility that a relaxing film around the droplet exists indicates that the electrical behavior of the emulsion will be quite complex, and that for all practical purposes it is impossible to derive reliable information about the relative permittivity of supercooled water from an analysis of the complex permittivity of an emulsion. However, it is apparent that useful information could be obtained if the individual relaxations of each *RC* element could be resolved, or if the effects of the emulsifier layer could be suppressed by an appropriate form of data analysis. Both of these objectives can be achieved if the data are analysed in terms of the complex inverse relative permittivity, or electric modulus M^*.[13-15] The imaginary component of this quantity M'' is given by

$$M''=\frac{\epsilon''}{\epsilon'^2+\epsilon''^2} \quad , \tag{8}$$

where ϵ'' now includes the contribution from the dc conductivity. It can be shown that each parallel *RC* combination gives rise to a Debye form for M'',

$$M''=\frac{C_0}{C}\left(\frac{RC}{1+\omega^2R^2C^2}\right) \ , \tag{9}$$

where C_0 is the vacuum capacitance between the measuring electrodes. If a number of these *RC* elements are arranged in a series the corresponding number of peaks in M'' is observed as a function of frequency, because M^* is essentially an impedance formalism.[15] This is illustrated in Fig. 1(b), where the spectrum of M'' is shown for the equivalent circuit shown in Fig. 1(a).

There are two features of Fig. 1(b) to which attention is drawn. Firstly, the maximum values of M'', M''_{max}, occur at frequencies equal to the inverse *RC* relaxation times of each individual element, in contrast with the maximum in ϵ'' which occurs at a frequency given by the inverse of an average of these relaxation times. Secondly, Eq. (9) indicates that the magnitudes of M''_{max} are determined by the reciprocal capacitances of each element. This is illustrated in Fig. 1(b) by the difference in peak heights, corresponding to the different capacitances given in Fig. 1(a). This is an important feature because the layer around the water droplets probably has a high capacitance as a result of its thinness, so that the spectrum of M'' might be expected to suppress the associated relaxation and therefore reflect only the relaxation of the water droplet. This expectation is, of course, dependent on the validity of the equivalent circuit used and in particular depends on the assumption that the impedance of the water droplet is in series with the emulsifier layer. Such an assumption is reasonable, however, since if the latter is thin any path around the droplet would have a large impedance compared with the path through the water. The best reason, however, for accepting the advantages of the modulus analysis is the good agreement which is obtained between literature data and data derived from the spectra of M''.

With these assumptions, data analysis using M'' is as simple as the analysis discussed above using ϵ'' is complex. The capacitance of the water droplet is taken to be directly proportional to the relative permittivity ϵ_0 of water and inversely proportional to M''_{max}, the proportionality constants being fixed by the known permittivity at 0 °C. The conductivity σ_0 is similarly determined by f_{max} and the derived value of ϵ_0. The specific equations are

$$\epsilon_0=K/M''_{\text{max}} \quad , \tag{10}$$

$$\sigma_0=2\pi e_0\epsilon_0 f_{\text{max}} \quad . \tag{11}$$

For the emulsion data reported here, K in Eq. (10) is 2.25, and C_0 in Eq. (9) is 1.37 pF.

EXPERIMENTAL

The emulsions were prepared in essentially the manner described previously,[17] with the volume fraction of water (0.3) being high for reasons given in the introduction. Although the mixture of heptane and carbon tetrachloride reduced settling below 0 °C, the addition of the latter lead to a decrease in emulsion stability above 0 °C, and a deterioration in the propensity for supercooling. Reproducibility was therefore a serious problem. The reliability criterion adopted was agreement between data taken at 0 °C before and after excursions to lower temperatures. For one run, the agreement was 4% for the maxima in ϵ'' and M'', and better than 0.1 log frequency units for the positions of these maxima. This implies very limited crystallization. The data derived from this run were then used to calibrate data from one other run, for which data at 0 °C were not taken, but which were acceptable down to −25 °C before crystallization apparently occurred. Large deviations of the temperature dependences of ϵ_0 and f_{max} from the "reference" run were taken as evidence for crystallization, and such data were discarded. This method of identifying incorrect data was necessary because crystallization occurred slowly, presumably as a result of nucleating motes being distributed over many droplets and variations in their effectiveness as nucleating agents. As a result, the onset of crystallization did not manifest itself clearly while an experiment was being conducted.

Data were taken over the frequency range 5×10^4–3×10^6 Hz using a Wayne–Kerr SR268 source and detector unit. A general purpose all metal cell, described elsewhere[16] was used. Typical uncertainties in R, C, and f at the loss maxima were ca. 1%. Temperatures were measured with a calibrated chromel-alumel thermocouple situated close to the electrodes. During a typical experiment temperature drift was ca. 1 °C or less, but the temperatures quoted in the results are those at which ϵ'' and M'' passed through their maxima and have an estimated uncertainty of 0.1 °C.

RESULTS

The temperature dependences of the observed dielectric loss and modulus spectra are shown in Fig. 2. The decreasing magnitude of ϵ''_{max} with decreasing temperature, which has been discussed above, is seen to be quite marked. The temperature dependence of f_{max}, on the other hand, is of the expected magnitude and is in the correct direction. The peaks for both M'' and ϵ'' are approximately Debye-like, their half widths being 1.31 ± 0.05 decades compared with the Debye width of

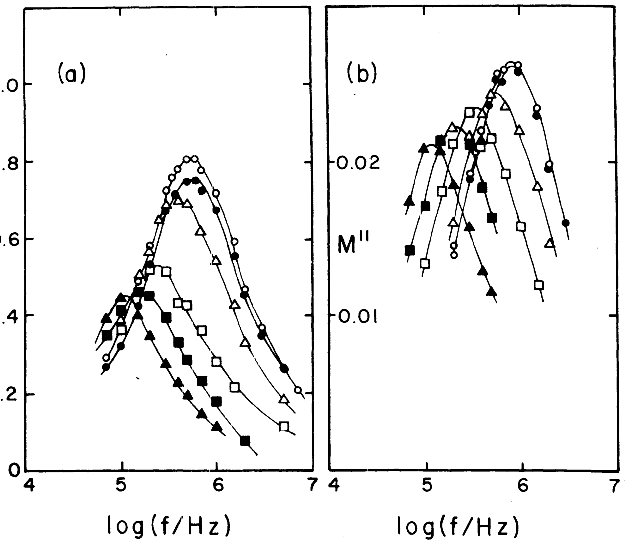

FIG. 2. (a) Observed dielectric loss of water emulsions as a function of frequency and temperature; (b) Observed electric loss modulus of water emulsions as a function of frequency and temperature. ○ 0 °C at beginning of run 1; ● 0 °C at end of run 1; △ −9.8; □ −21.4; ■ −28.8; and ▲ −35.0. Results of run 2 are omitted to avoid crowding.

1.15 decades. Some of this departure from Debye behavior can be attributed to temperature drift. The parameters of interest for these spectra are collected in Table I, together with the quantities derived from them. Values of ϵ_0 and σ_0 were derived from the raw data using Eqs. (10) and (11), respectively. (See "Note added in proof" above concerning accord with other data).

The temperature dependence of ϵ_0 was fitted to the following two three-parameter equations,

$$\epsilon_0 = a_0 + a_1 t + a_2 t^2 \ , \tag{12}$$

where t is in °C, and

$$\epsilon_0 = A_\epsilon (T/T_s - 1)^{\gamma_\epsilon} \tag{13}$$

where T is in °K and $T_s = 228$ K.[2]

TABLE I. Experimental and derived data.

Temperature (°C)	$\epsilon''_{\max}$	$M''_{\max} \times 10^2$		$\log_{10} f_{\max}$	ϵ'_0 from $M''_{\max}$	$\epsilon_0 f_{\max} \times 10^{-7}$
$-0.3^{a,c}$	0.810	2.63	2.57^e	5.90	87.7^g	6.9
$-0.5^{a,d}$	0.754	2.52		5.90		
-9.8^a	0.701	2.44		5.70	92.4	4.6
-16.0^b	0.530	2.37^f		5.58	95.1^h	3.6
-21.4^a	0.520	2.30		5.50	98.0	3.1
-22.3^b	0.520	2.30		5.51	98.1	3.1
-28.8^a	0.460	2.22		5.32	101.5	2.1
-35.0^a	0.444	2.12		5.06	106.3	1.2

[a] Run 1.
[b] Run 2.
[c] Beginning of run.
[d] End of run.
[e] Average of values observed at −0.3 and −0.5 °C before and after excursion to −35 °C.
[f] Fixed by smoothed data from run 1.
[g] Fixed by literature value.
[h] Fixed by smoothed data from run 1.

The temperature dependence of $\epsilon_0 f_{\max}$ [equal to $\sigma_0 / 2\pi e_0$, Eq. (12)] was also fitted to two similar three-parameter equations, Eqs. (14) and (15).

$$\log_{10} \epsilon_0 f_{\max} = A_0 + A_1 (1/T) + A_2 (1/T)^2 \ , \tag{14}$$

$$\epsilon_0 f_{\max} = A_\sigma (T/T_s - 1)^{\gamma_\sigma} \ , \tag{15}$$

where again $T_s = 228$ K. To compare the conductivity data with diffusivity data, the quantity $\epsilon_0 f_{\max} T$ was also fitted to an equation of the form (15). The least squares values of the parameters of these equations are given in Table II.

The temperature dependences of ϵ_0 and σ_0 are shown in Figs. 3(a) and (b), respectively, together with the indicated best fit equations. The errors, estimated as ± 2%, are based on the reading errors for the raw R, C, and f data, and in the case of ϵ_0 the extra uncertainty in $M''_{\max}$ due to partial crystallization. It is apparent that the critical exponent expressions give fits which are within experimental uncertainty. In the case of the conductivity, the Eq. (15) description of the temperature dependence is as good as that of the quadratic equation. Although a better fit to the ϵ_0 data could be obtained by reducing the parameter T_s, this was not attempted.

For comparison, the behavior of ϵ_0 for ice is included in Fig. 3(a). In the frequency range of this study, how-

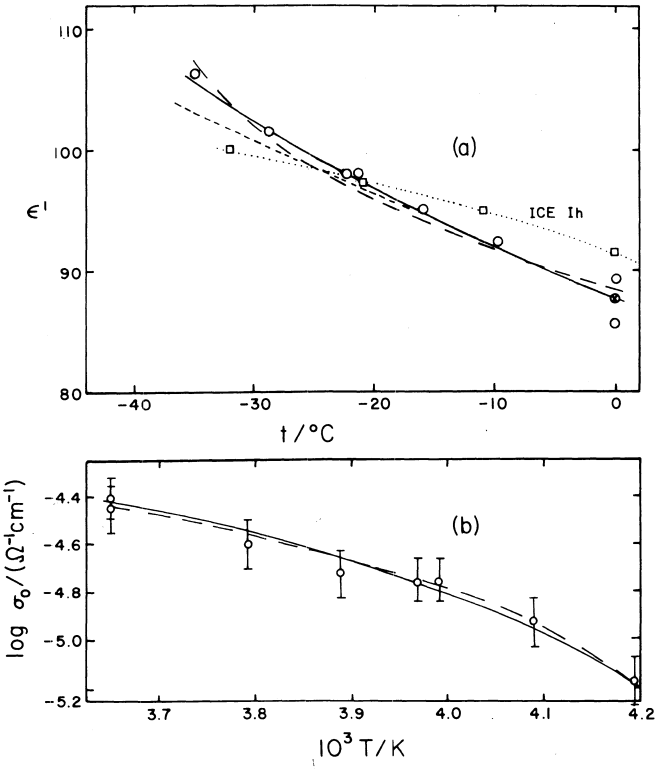

FIG. 3. (a) Temperature dependences of relative permittivity. ○ data derived from Eq. (10). Solid line is least-squares quadratic, long dash line is least-squares critical exponent [Eq. (13)] short dash line is literature extrapolation, and dotted line is literature data for ice Ref. 12. On the scale of this figure, the two literature equations for water are indistinguishable. (b) Temperature dependence of conductivity. ○ data derived from Eq. (11). Solid line is least-squares quadratic, long dashed line is least squares critical exponent, Eq. (15).

TABLE II. Least squares parameters for the relative permitivity and conductivity.

Quantity	Quadratic parameters [Eqs. (12), (14)]			Critical Exponent Parameters [Eqs. (13), (15)]		
	a_0, A_0	a_1, A_1	a_2, A_2	A_ϵ, A_σ $P_{1,2}$	γ_ϵ, γ_σ	T_c (K)[a]
ϵ_0	87.9	−0.3849	+0.00372	72.94	−0.1256	228
$\epsilon_0 f_{\max}$	−4.1525	7295.6	-1.996×10^6	4.003×10^6	1.1334	228
$T\epsilon_0 f_{\max}$		···		1.228×10^{11}	1.216	228

[a] Fixed.

ever, ice would exhibit its "infinite" frequency dielectric constant which is small and temperature independent. Any corrections for the effect of partial crystallization at the lowest temperatures would therefore raise ϵ_0 for water and thus improve the fit to Eq. (13).

DISCUSSION

Extrapolations of two literature equations[18,19] for ϵ_0 to subzero temperatures are also shown in Fig. 3. Down to ca. −25 °C they are indistinguishable within experimental error from Eqs. (12) and (13). This, together with the agreement between the observed temperature derivative of ϵ_0 at 0 °C, −0.385, and the literature values of −0.401[18] and −0.403,[19] provides strong support for the validity of Eq. (10). The activation energy for the conductivity at 0 °C, calculated from Eqs. (11) and (14), is 3.5 kcal mole^{-1}. This is typical of the values characterizing the limiting equivalent conductances[20] of ions such as Na^+ (3.5 kcal mole^{-1}) and Cl^- (3.3), and higher than those of H^+(2.1) and OH^- (2.8). The conductivity calculated from Eq. (11) is 3.5×10^{-5} $\text{ohm}^{-1}\,\text{cm}^{-1}$ at 0 °C, which is that of $\sim 3\times10^{-4}$ molar solution of NaCl at 25 °C. This concentration of NaCl is sufficiently low to warrant both the use of the limiting conductance in comparing activation energies, and also the interpretation that the emulsified water is contaminated to a rather small extent with electrolyte, probably by the emulsifying agent or impurities in it.

In view of the experimental difficulties and the assumptions used in the data analysis, the reasonableness of the above results must be considered somewhat fortunate. However, we will accept the results at face value, and will permit ourselves some comments on the meaning of the equation fits and some comparisons of the critical exponents with those characterizing other properties.

A divergence of ϵ_0 at T_s indicated by conformity to Eq. (13) would imply a ferroelectric state for $T < T_s$, the possible connection of which with the other observed supercooled water anomalies has been mentioned by Stillinger.[21] The critical exponent we obtain from the Eq. (13) fit (−0.126) is, however, the smallest for any property of water so far, and is so much less than that associated with familiar ferroelectric phase transitions ($\gamma = 1.0$, Curie–Weiss Law) that the anomalous dipole-alignment aspect of water in this regime should probably be regarded as incidental to, rather than causative of, the other anomalies.

Although the conductivity derived from the present data is not that of pure water, ion motions do reflect the dynamics of the solvent water since the product $\lambda_0\eta_0$, where λ_0 and η_0 are the limiting equivalent conductance and viscosity, respectively, is "very nearly constant over a fair range in temperature."[22] A valid comparison with other transport properties can therefore be made. The best fit critical exponent for the conductivity σ_0 is 1.133, and that for $\sigma_0 T$ ($\propto D$) is 1.216. These are to be compared with 1.454 for the diffusivity[5] over the range −9 to −31 °C and 1.476 for the shear viscosity[7] over the range from 0 to −24 °C. These phenomenologically related quantities encompass a group of critical exponents (1.30 ± 0.17) which is separated from those of other quantities. The closest exponents are 1.717 for the proton spin–lattice relaxation time[2] and −0.349 for the isothermal compressibility[2] [Although the ratio of the shear to bulk viscosity has a critical exponent of −0.68,[6] this is deduced from data at relatively high temperatures (−8 to +40 °C). In addition, this exponent reflects the difference in the two viscosities, rather than a single property.].

CONCLUDING REMARKS

The use of M'', rather than ϵ'', provides an enormous simplification of data analysis for systems in which interfacial effects are important. This is particularly well illustrated in the present case, where the correct temperature dependence of the permittivity can only be obtained when the data are analysed in terms of M''. It would appear that the uncertainties in the data reported here are due primarily to uncertainties in the raw data rather than in the method of data processing. It is therefore feasible that substantially more accurate permittivity and conductivity data could be obtained from measurements of the Maxwell–Wagner effect in water emulsions under more reproducible conditions.

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