New permittivity measurements of seawater

W. Ellison,[1] A. Balana,[1] G. Delbos,[1] K. Lamkaouchi,[2]
L. Eymard,[3] C. Guillou,[3] and C. Prigent[4]

Abstract. We have measured the permittivity of representative samples of natural seawater, synthetic seawater, and aqueous NaCl solutions over the frequency range 3–20 GHz, in 0.1-GHz steps and over the temperature range −2°–30°C in 1° steps. Additional measurements have been made at spot frequencies (23.8, 36.5, and 89 GHz) and at selected temperatures between −2° and 30°C. The data from these measurements have allowed us to deduce an interpolation function for $\varepsilon(\nu, t, S)$ in the ranges $2 \le \nu \le 20$ GHz, $-2° \le t \le 30°C$, and $20\permil \le S \le 40\permil$ with a precision of 1%. If the frequency range is extended up to 40 GHz, the precision of the interpolation function is about 3%. The data have also allowed us to compare the permittivities of natural seawater, synthetic seawater, and aqueous NaCl solution with the same salinities. Natural and synthetic seawater have the same permittivities within a 1% experimental error estimate. An aqueous NaCl solution has a significantly different permittivity (up to about 6% difference, depending upon the frequency and temperature).

1. Introduction

For microwave remote sensing applications over the ocean using radars and radiometers, a precise knowledge of the emissivity and reflectivity properties of the sea surface is required. The dielectric permittivity of seawater $\varepsilon(\nu, t, S)$ for a frequency ν, temperature t, and salinity S is a vital parameter in all models describing the interaction of a wind-roughened sea surface with microwave radiation.

The main objectives of the research program were to (1) deduce an interpolation function for $\varepsilon(\nu, t, S)$ with a precision good enough to satisfy the technical improvements in radiometric sensitivities for use in radiative transfer models in the frequency range 1–100 GHz and (2) elucidate the role of the ionic content and the organic matter upon the permittivity of seawater. An application of the proposed permittivity interpolation model to actual radiometer data is given by *Guillou et al.* [this issue].

2. Literature Data and Current Permittivity Models for Seawater and Salt Water

Authors who describe models for the permittivity of seawater and aqueous saline solutions are *Stogryn* [1971], *Klein and Swift* [1977], and *Aggarwal and Johnston* [1988]. The model of *Liebe et al* [1991] is for pure water, but it is often used to represent the permittivity of seawater for frequencies around 100 GHz. The hypothesis is that at high frequencies the ionic content of seawater plays only a small role and that there should be very little difference between seawater and pure water. The validity of this hypothesis depends entirely upon what is considered an acceptable precision for the permittivity values of seawater.

The goal of such models is to provide the permittivity and conductivity of seawater at any frequency as a function of the "salinity" and temperature. Such a model has to be based upon experimental data. We have found only three authors who report permittivity measurements of natural seawater: *Ho and Hall* [1973], *Ho et al.*, [1974], and *Blue* [1980]. The first two give data for the frequencies 1.43 and 2.653 GHz, the temperatures 5°, 10°, 20°, and 30°C, and for a representative range of salinities. The third reports on measurements at frequencies of 97, 103.8, 135.6, and 183.3 GHz and over the temperature range 0°–60°C. However, numerical data are given only for 20°C.

In spite of the small number of authors concerned

[1] Laboratoire de Physique des Interactions Ondes-Matière, Université Bordeaux, Talence, France.
[2] Equipe de Spectronomie, Département de Physique, Faculté des Sciences, Meknès, Morocco.
[3] Centre d'étude des Environnements Terrestre et Planétaire, Centre Universitaire, Vélizy, France.
[4] Goddard Institute for Space Studies, New York.

with the dielectric properties of seawater, three important observations emerge.

1. At 1.4, 2.653, and around 100 GHz, untreated (i.e., "as is") seawater samples do not change their dielectric properties over a period of several months. Any ionic changes, due to organic component decomposition, should be readily visible at the "low" frequencies. No such changes were observed. Thus any possible biological decomposition seems to have no effect upon the permittivity.

2. The dielectric properties of seawater depend only upon the temperature and the inorganic "ionic" content.

3. At frequencies around 100 GHz the variations in the ionic content of seawater have a very small effect upon permittivity.

These observations are also confirmed by our measurements.

In view of the paucity of data for natural seawater, model makers were forced to use permittivity data of aqueous solutions of NaCl, KCl, etc. These salts are important constituents of seawater, and it was reasonable to suppose that their dielectric behavior was similar to that of seawater. The authors who gave numerical data are *Cooper* [1946], *Hasted et al.* [1948], *Haggis et al.* [1952], *Lane and Saxton* [1952], *Saxton and Lane* [1952], *Hasted and El Sabeh* [1953], *Weiss et al.* [1965], *Barthel et al.* [1970], *Kumar* [1979], *McAvoy and Buckmaster* [1984], *Winsor and Cole* [1985], *Johri et al.* [1991], *Han et al.* [1991], and *Buchner et al.* [1994]. A critical analysis of these articles is given by *Ellison et al.* [1995, 1996b]. The conclusions of this analysis are that the permittivity measurements of aqueous ionic solutions are either at a fixed temperature (often 25°C) over a concentration range with relatively large steps (0.1 N or even 1 N) or at a variable temperature (often in 10° steps) and at a unique concentration (or for very few concentrations). Also, most of the data are for frequencies less than 10 GHz. There are one or two other spot frequencies (23 GHz, 48 GHz, etc.) in the older and relatively inaccurate data. The only study over a large frequency range (5–89 GHz) is that of *Buchner et al.* [1994], but this is for an aqueous KF solution at a temperature of 25°C. The role of KF in seawater is probably negligible. The typical study, for a given concentration and temperature, is at two or three spot frequencies. Finally, there is no comprehensive study for any aqueous ionic solution for variable concentration, temperature, and frequency.

For oceanographic purposes the relevant temperature range is −2°–30°C, and the relevant concentration range is 0.5 N to 0.8 N. No published data correspond to these temperatures and concentrations.

In spite of the lack of experimental data, numerous authors have attempted spectral analyses under more or less plausible hypotheses. The standard supposition is that for a fixed temperature t of an aqueous saline solution of "salinity" S, the permittivity is described by a Debye function:

$$\varepsilon(\nu, t, S) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 - j2\pi\tau\nu} + j\,\frac{\sigma}{2\pi\nu\varepsilon^*}$$

where $\varepsilon_0(t, S)$, $\varepsilon_\infty(t, S)$ are the static and high-frequency dielectric constants; $\tau(t, S)$ is the relaxation time in seconds; $\varepsilon^* = 8.8419 \times 10^{-12}$ F/m; $\sigma(t, S)$ is the ionic conductivity of the disolved salts in mhos/m; and ν is the electromagnetic frequency in herz.

The Debye parameters $\varepsilon_0(t, S)$, $\varepsilon_\infty(t, S)$, and $\tau(t, S)$ depend upon the temperature t and the concentration S of the ionic salts. This concentration can be represented in terms of salinity, chlorinity, normality, etc. We shall use the notion of salinity to measure the concentration of the ionic salts, i.e., the total weight of the disolved salts in grams per kilogram of solution.

The parameter $\varepsilon_\infty(t, S)$ is, in reality, a "fudge factor." It is determined so that the experimental data fit a Debye function "as best as possible." If the data followed exactly a Debye relaxation, then there is a physical interpretation as the "high-frequency" permittivity, where high frequency is way beyond the ultraviolet! As real liquids rarely follow a Debye relaxation over such a large frequency range, the $\varepsilon_\infty(t, S)$ obtained by a curve fitting procedure on data measured at frequencies less than 20 GHz has no physical significance.

For pure water it is true that over a restricted frequency range, up to about 40 GHz, it is possible to obtain very close approximations to the experimental data via a simple Debye function; the parameters so obtained will depend upon the temperature (see *Kaatze* [1989] and *Ellison et al.* [1996] for more detailed information). It is also true that as the temperature increases (above 25°C) the Debye function approximates the experimental data more closely. However, a careful analysis of the mass of permittivity data for water and recent very precise measurements by *Barthel et al.* [1991] suggest that water does not follow a Debye relaxation over the

frequency range 0–100 GHz and that the deviation from Debye behavior is more pronounced as the temperature decreases to zero. Our measurements of saline solutions indicate that they also have a behavior similar to that of pure water.

The assumption of a Debye model, together with relatively few frequency measurements, enables the extraction of a relaxation time and a static dielectric constant. Unfortunately, if one uses only two or three frequencies, the resulting Debye parameters are very sensitive to experimental errors in the data. For any individual article in which there are few frequency measurements, the calculated Debye parameters are certainly inaccurate. However, a qualitative picture does emerge, which is probably close to the truth.

For a fixed temperature t and variable salinity S, the Debye parameters are of the form

$$\varepsilon_{s\,\text{sol}}(t,\,S) = \varepsilon_{s\,\text{water}}(t) - \delta_1(t)S,$$

$$\tau_{\text{sol}}(t,\,S) = \tau_{\text{water}}(t) - \delta_2(t)S$$

The parameters δ_1 and δ_2 depend upon the solute and the temperature. The approximation seems to hold for moderate concentrations: $0 < c < 1$ mol/L. The salinity of natural seawater falls in this interval. For "high" salt concentrations the relation is no longer linear.

The published numerical data cannot be used to determine δ_1 and δ_2 as functions of t. However, the above linear law can be assumed to be valid with reasonable confidence.

3. Material and Methods

The primary object of the study was to measure the permittivity of natural seawater samples, collected in situ. Six types of natural seawater samples, covering the range of salinities found in the worlds oceans, were obtained with the help of oceanography colleagues. The samples came from the Mediterranean (latitude 42°35′35″N, longitude 00°03′13″W, salinity 38.024‰ and latitude 35°00′42″N, longitude 28°24′17″W, salinity 38.893‰); polar waters (latitude 80°00′00″N, longitude 01°34′56″W, salinity 30.255‰); the Atlantic-Gironde estuary (latitude 45°30′76″N, longitude 00°58′49″W, salinity 28‰ and latitude 45°30′76″N, longitude 00°52′76″W, salinity 23.2‰); and the Mid-Atlantic (latitude 44°10′30″N, longitude 14°23′16″W, salinity 35.725‰).

Our collection protocol was stringent: Use sterilized sample bottles with sealed caps, and keep the samples in constant refrigeration at 4°C. A certain number of the sample bottles were "stabilized" with an $HgCl_2$ solution. This kills any living organisms in the seawater.

With the original samples under strict control our intention was to study the effect of the organic content, storage time, and stabilizing upon the conductivity and permittivity.

The electrical conductivity of all the samples was measured using a standard conductance meter at temperatures between −2° and 30°C. The precision of the measurement was estimated to be about 1%. The permittivities of all the liquid samples were deduced by measuring a transmission coefficient of electromagnetic waves passing through a measuring cell containing the liquid trapped between two quartz windows. The apparatus used in the frequency range 3–20 GHz is "classic" and consists of (1) a Hewlett Packard 8510B vector network analyzer to measure transmission coefficients, (2) coaxial transmission measuring cells, constructed in our laboratory and designed specifically to optimize the determination of seawater permittivity, and (3) a custom-built thermostatic system which controls the temperature of the measuring cell and liquid sample to ±0.01°C. The experimental precautions which were taken (thickness of the measuring cells, thermal regulation, humidity control, etc.) to obtain a 1% experimental accuracy are described by *Ellison et al.* [1996].

For frequencies higher than 20 GHz we used a free-air propagation transmission method with a variable thickness sample cell. The apparatus used was an ABmm MVNA8-350 vector network analyzer to measure transmission coefficients. The measuring cell is a custom-designed variable-thickness cell. The physical characteristics can be precisely controlled (temperature to ±0.01°C, thickness of the liquid sample to ±1 μm). Technical experimental details of this novel method, which has an uncertainty of about 3% in the resulting permittivity values in the frequency range 30–110 GHz, are given by *Lamkaouchi et al.* [1997].

4. Seawater: Organic Content, Storage Conditions, and Temporal Stability

The organic content of seawater contains both dissolved and particulate matter (living cells, "plankton," etc., as well as solid components). The usual estimates for the density of the organic content of seawater [*Riley and Skirrow*, 1965] for most ocean areas are in the range 1.50–3.00 g/m^3.

A natural question to ask is, Does the organic content of natural seawater have a measurable influence upon its permittivity? To answer this question, we used samples of Atlantic seawater collected in the Gironde estuary. The principal chemical species in the sample corresponds to a typical seawater composition. Dissolved organic substances contained trace elements of principally organic nitrogen, phosphorus, various proteins, amino acids, etc., no doubt originating from agricultural fertilizers used in the coastal region. The suspended matter in the sample consisted of particles of organic origin and particles of inorganic origin. The organic particles included bacteria, fungi, phytoplankton, zooplankton, and detritus: the decomposition remains of marine organisms and humus substances. The inorganic suspensions consisted of various kinds of mineral particles derived from rock debris and clay transported by the river water. Trace elements of various complexes of metals, mercury, cadmium, etc., were detected. The particle sizes ranged from 1 μm up to 50 μm. It was estimated that 14% of the particulate suspensions were of organic origin. The concentration of the particulate suspension in the sample was 5.75 g/m^3.

We measured the permittivity of an untreated sample within 12 hours of collection, at a temperature of 20°C in the frequency range 3–20 GHz. Any effect due to the organic matter should be visible here. The sample was then filtered to remove all the particulate matter greater than 1 μm and the permittivity remeasured. There was no difference, within the 1% experimental error, between the two permittivity values.

As there can be a considerable delay between the collection of, say, polar seawater and the laboratory permittivity measurements, an important question to be answered was, Does the permittivity of the seawater samples change over time when the samples are kept in "ideal" conditions (i.e., at 4°C, in the dark, and in sealed sterile bottles)?

To test the effect of the time element upon the sample permittivity, we carried out the following two experiments: (1) Once a month, between June 1995 and June 1996, we opened a fresh bottle of Mediterranean water (salinity 38.024‰) and measured the permittivity at 25°C and over the frequency range 3–20 GHz. (2) Using the same opened bottle (kept stored at 4°C), we also remeasured the permittivity once a month at 25°C and over the frequency range 3–20 GHz. The measured permittivities were always the same, within the 1% experimental error.

As we had no a priori reason to suppose that the

living organisms in seawater would not affect the permittivity over a timescale of several months we "stabilized" or "poisoned" several of the seawater samples with an HgCl$_2$ solution when they were collected. This kills any living organisms in the water. It was important to find out whether this procedure was, in fact, necessary and whether it affects the permittivity of the samples.

Each poisoned seawater bottle sample was compared with an unpoisoned bottle of the same seawater sample. The conductivity of the poisoned sample was always slightly higher (about 1%) than the unpoisoned bottle. It is possible that this is due to the chlorine ions introduced in the sample by the HgCl$_2$. However, the difference is very close to the experimental uncertainty of the conductance meter. The effect of the poison upon the permittivity was measured at 25°C and over the frequency range 3–20 GHz. The difference between the permittivities of poisoned and unpoisoned samples was always less than 1%, which is within the experimental uncertainty. Thus the conclusions of this investigation are the following:

1. The influence of the organic content, in quantities which occur in natural conditions, is not detectable with our measuring system, which is designed to have an experimental accuracy of about 1% for frequencies less than 20 GHz.

2. Seawater samples, stored in the dark at 4°C, are stable, as far as their permittivity is concerned, for at least 12 months.

3. It is not necessary to poison the seawater samples to conserve them for 12 months.

These conclusions are also in accordance with the observations of Ho and Hall [1973], Ho et al. [1974], and Blue [1980].

4.1. The Conductivity Data for Seawater

The conductivity of seawater is a function of the temperature and the salinity. We denote it by $\sigma(t, S)$. For the samples under investigation we have $-2° \leq t \leq 30°$ and $20‰ \leq S \leq 40‰$. Our intention is to provide an interpolation function for $\sigma(t, S)$ within the above ranges for use in the Debye permittivity interpolation model.

For a fixed temperature and for salinities in the range $20‰ \leq S \leq 40‰$, the conductivity $\sigma(t, S)$, in siemens/m, is a linear function of S, as shown in Figure 1. This linearity over a relatively small salinity range is reasonable, since the conductivity is proportional to the number of free ions in the water and the
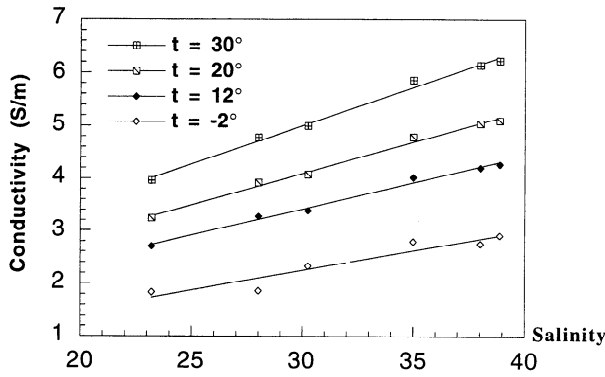
Figure 1. Conductivity as a function of salinity at four typical temperatures.

number of free ions is almost directly proportional to the salinity. For a fixed salinity the variation of the conductivity as a function of temperature is not linear. A typical example is shown in Figure 2.

A straightforward regression analysis on our data for all the seawater samples gives us the interpolation function for the conductivity of seawater as a function of the temperature t and salinity S:

$$\sigma(t, S) = c_1(t) + c_2(t)S$$

where

$$c_1(t) = 0.086374 + 0.030606t - 0.0004121t^2$$

$$c_2(t) = 0.077454 + 0.001687t + 0.00001937t^2$$

The average difference between the interpolated and the measured values of the seawater samples was less
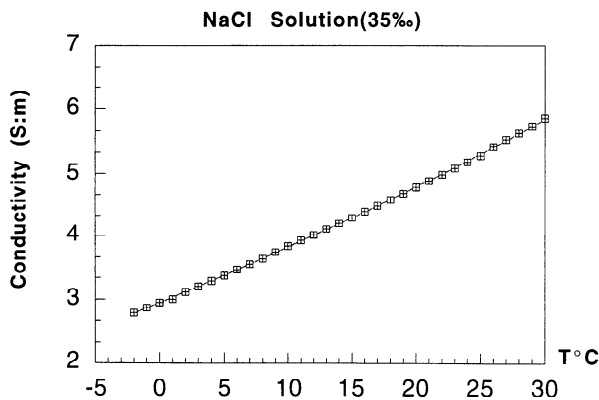

Figure 2. Conductivity of a 35‰ saline solution as a function of temperature.

than 1%, which corresponds to the experimental error of the conductance meter and is perfectly adequate for use in a permittivity model.

4.2. The Permittivity Data for Seawater

We measured the permittivity of each of the six natural seawater samples at 201 equally spaced frequencies in the range 3–20 GHz and at 1° temperature steps in the interval 2°–30°C, with a precision of about 1%. The permittivities of the same samples were also measured at 23.8, 36.5, and 89 GHz and at temperatures of −2°, 12°, 20°, and 30°C, with an estimated precision of 3%. The raw numerical data and many graphical representations are given by *Ellison et al.* [1996a]. We report the main conclusions here.

1. For a fixed temperature and a fixed salinity the permittivity of natural seawater in the frequency range 3–20 GHz is very closely represented by the simple Debye model. The average percentage difference between the measured values and those calculated from a "best least squares fit" to the Debye model is always within the 1% experimental uncertainty.

2. For each fixed temperature, the Debye parameters $\tau(t, S)$, $\varepsilon_0(t, S)$ calculated for each of the six salinities of the seawater samples are linear functions of S.

Our goal is to obtain polynomial interpolation functions for $\tau(t, S)$, $\varepsilon_0(t, S)$, and $\varepsilon_\infty(t, S)$ as functions of t and S in the Debye model. With these functions and the interpolation formula for $\sigma(t, S)$ given in section 4.1 one can then calculate $\varepsilon(\nu, t, S)$ for any value of ν, t, and S in the interpolation ranges.

For frequencies ν in the range $3 \leq \nu \leq 20$ GHz, temperatures t in the range $-2° \leq t \leq 30°$C, and salinities S in the range $20‰ \leq S \leq 40‰$, the permittivity of seawater $\varepsilon(\nu, t, S)$ is given with a precision of about 1% by

$$\varepsilon'(\nu, t, S) = \varepsilon_\infty(t, S) + \frac{\varepsilon_0(t, S) - \varepsilon_\infty(t, S)}{1 + 4\pi^2\nu^2\tau^2(t, S)}$$

$$\varepsilon''(\nu, t, S) = \frac{(\varepsilon_0(t, S) - \varepsilon_\infty(t, S))2\pi\nu\tau(t, S)}{1 + 4\pi^2\nu^2\tau^2(t, S)} + \frac{\sigma(t, S)}{2\pi\varepsilon^*\nu}$$

where ν is the frequency in hertz and $\varepsilon^* = 8.8419 \times 10^{-12}$ F/m.

If we write

$$\varepsilon_0(t, S) = a_1(t) + Sa_2(t)$$

$$\tau(t, S) = b_1(t) + Sb_2(t)$$

then for each t in the interval $-2 \leq t \leq 30°C$ we calculated the coefficients $a_i(t)$ and $b_i(t)$ for $i = 1, 2$ by a least squares regression analysis. The final step is to interpolate the parameters $a_i(t)$, $b_i(t)$, and $c_i(t)$ by ad hoc polynomials, as we have no compelling physical model to use. The results are

$$a_1(t) = 81.820 - 6.0503 \times 10^{-2}t - 3.1661 \times 10^{-2}t^2$$
$$+ 3.1097 \times 10^{-3}t^3 - 1.1791 \times 10^{-4}t^4 + 1.4838$$
$$\times 10^{-6}t^5$$

$$a_2(t) = 0.12544 + 9.4037 \times 10^{-3}t - 9.5551 \times 10^{-4}t^2$$
$$+ 9.0888 \times 10^{-5}t^3 - 3.6011 \times 10^{-6}t^4 + 4.7130$$
$$\times 10^{-8}t^5$$

$$b_1(t) = 17.303 - 0.66651t + 5.1482 \times 10^{-3}t^2 + 1.2145$$
$$\times 10^{-3}t^3 - 5.0325 \times 10^{-5}t^4 + 5.8272 \times 10^{-7}t^5$$

$$b_2(t) = -6.272 \times 10^{-3} + 2.357 \times 10^{-4}t + 5.075$$
$$\times 10^{-4}t^2 - 6.3983 \times 10^{-5}t^3 + 2.463 \times 10^{-6}t^4$$
$$- 3.0676 \times 10^{-8}t^5$$

For each of the different salinities the behavior of $\varepsilon_\infty(t, S)$ is similar: a decrease with increasing temperature, up to about 15°C, followed by an increase with increasing temperature and no dependence upon S. We pooled all the data and calculated a polynomial interpolation function for $\varepsilon_\infty(t, S)$. It is

$$\varepsilon_\infty(t, S) = 6.4587 - 0.04203t - 0.0065881t^2$$
$$+ 0.00064924t^3 - 1.2328 \times 10^{-5}t^4 + 5.0433$$
$$\times 10^{-8}t^5$$

The conductivity term is given by

$$\sigma(t, S) = c_1(t) + c_2(t)S$$

$$c_1(t) = 0.086374 + 0.030606t - 0.0004121t^2$$

$$c_2(t) = 0.077454 + 0.001687t + 0.00001937t^2$$

4.3. Seawater Permittivity in the Range $20 \leq v \leq 37$ GHz

The extremely good representation of the permittivity data in the frequency range $3 \leq v \leq 20$ GHz

Table 1. Comparison Between Measured and Extrapolated Permittivities at 23.8 GHz and Salinity 38.893

Temperature	ε' Extrapolated	ε' Measured	ε'' Extrapolated	ε'' Measured
-2°C	14,76	15,90	25,00	24,72
12°C	23,00	23,83	32,27	32,07
20°C	28,88	29,13	34,18	34,14
30°C	34,83	35,09	34,13	34,52

(less than 1% difference) means that one can extrapolate the model outside this range with perhaps some loss in precision. We compared the extrapolated permittivity values with the measured values at 23.8, 36.5, and 89 GHz for the temperatures $-2°$, $12°$, $20°$, and $30°C$. The results, at 23.8 and 36.5 GHz, for a typical salinity are given in Tables 1 and 2.

In all cases the differences between the calculated and the measured values were, on average, less than the 3% experimental uncertainty. Since the four temperatures and the salinities are fairly evenly spread over realistic seawater values, we feel that the extrapolated permittivities will be equally valid for any temperature and salinity in the seawater ranges. Thus the Debye model given in section 4.2 can be used to calculate the permittivity of seawater in the ranges $20 \leq v \leq 40$ GHz, $20\%o \leq S \leq 40\%o$, and $-2° \leq t \leq 30°C$ with a precision of about 3%.

4.4. Seawater Permittivity at 89 GHz

For a fixed temperature we found no significant variation of the permittivity of natural seawater as a function of the salinity in the range $20\%o \leq S \leq 40\%o$. The measured and extrapolated permittivities are given in Table 3.

We see that the difference between the measured and extrapolated values can be as high as 20%, which is much larger than our supposed 3% experimental uncertainty. There are two possible causes for this deviation: (1) The experimental values at 89 GHz are incorrect. (2) The single Debye relaxation model,

Table 2. Comparison Between Measured and Extrapolated Permittivities at 36.5 GHz and Salinity 38.893

Temperature	ε' Extrapolated	ε' Measured	ε'' Extrapolated	ε'' Measured
-2°C	10,27	10,83	17,36	17,57
12°C	14,43	15,01	24,34	24,24
20°C	18,40	18,91	27,37	27,78
30°C	23,45	23,32	29,02	30,03

Table 3. Measured and Extrapolated Permittivity of Seawater at 89 GHz

Temperature	89 GHz Measured		89 GHz Extrapolated	
	ε'	ε''	ε'	ε''
30°C	9.46 ± 0.28	16.52 ± 0.50	11.33	14.81
20°C	8.81 ± 0.26	14.25 ± 0.42	8.78	13.15
12°C	8.09 + 0.24	12.33 + 0.37	7.51	11.12
−2°C	6.66 ± 0.20	9.44 ± 0.28	7.17	7.39

established over the frequency range 3–20 GHz, is not valid for "high" frequencies.

In order to test our experimental method we measured the permittivity of pure water at frequencies close to 89 GHz and at temperatures for which there are measurements in the scientific literature. There are data at 90 GHz (Table 4) for pure water, reported by *Richardson and Sheppard* [1991]. Their claimed experimental error is "about" 3% or 4%.

Our values were always within the claimed experimental errors of these authors, and we feel that our measurements of saline solutions, which do not differ substantially from pure water, as far as experimental difficulties are concerned, are correct within the claimed error estimate of 3%. The difference between the extrapolated values and our measured values for the seawater samples is greater than our estimated experimental error. We believe that the single Debye model is not valid for frequencies greater than 40 GHz.

There is some independent experimental evidence that for pure water the Debye model is not valid above 40 GHz. *Barthel et al.* [1990, 1991, 1992] report on the necessity of an additional Debye relaxation term in order to account for the permittivity of pure water for frequencies up to 90 GHz at a temperature of 25°C. Earlier, *Grant and Sheppard* [1974] found

Table 4. Measured and Literature Values of Permittivity of Pure Water at 90 GHz

Temperature	PIOM		Richardson and Sheppard [1991]	
	ε'	ε''	ε'	ε''
0°C	7.1	9.4	6.7	9.2
20°C	8.5	13.8	8.0	14.0
25°C	8.8	15.3	8.70	15.2
30°C	9.1	16.1	9.4	16.8

PIOM, Laboratoire de Physique des Interactions Ondes-Matière.

that a better fit to the experimental data for the permittivity of pure water "around" 4°C could be obtained by invoking a second Debye relaxation term with a high relaxation frequency. Our measurements confirm these observations and indicate that the divergence from Debye behavior is even more pronounced at "low" temperatures, i.e., in seawater conditions.

4.5. Seawater Permittivity at 89 GHz as a Function of Temperature

In view of the above observations we cannot give an adequate interpolation function for $\varepsilon(\nu, t, S)$ over the frequency range $40 \leq \nu \leq 100$ GHz without having new measured permittivity data. However, we can give an interpolation function at 89 GHz over the temperature range $-2° \leq t \leq 30°C$. The variation in the permittivity of seawater due to salinity changes is less than 3%, as is the difference between the permittivities of seawater and an aqueous NaCl solution with a salinity of 35‰. Thus we can combine the seawater data with the data of *Lamkaouchi et al.* [1997], in which the permittivity of such a solution was measured in 1° steps over the range 0°–25°C. The resulting interpolation formula, accurate to within 3%, is

$$\varepsilon'(89, t) = 6.9637 + 0.049373t + 0.0038553t^2$$
$$- 0.000090918t^3$$

$$\varepsilon''(89, t) = 9.9715 + 0.19710t - 0.00082745t^2$$
$$+ 0.0000064008t^3$$

5. Seawater, Aqueous NaCl Solutions, and Synthetic Seawater

An important point which seems never to have been elucidated in the literature is the relationship between the permittivity of natural seawater and an aqueous NaCl solution of the same salinity. In the current permittivity models the two sets of permittivity data are usually all mixed together, despite the observations of *Ho and Hall* [1973] and *Ho et al.* [1974], who found that NaCl solutions and natural seawater of the same salinity do not have the same permittivity at 1.43 GHz and 2.653 GHz, and *Weyl* [1964], who gives different interpolation functions for the conductivity of natural seawater and NaCl solutions as a function of temperature and salinity. This state of affairs was no doubt due to the quasi total

Table 5. Conductivity as a Function of Temperature

Temperature	Seawater	Synthetic Seawater	NaCl Solution
30°C	5.672	5.775	5.861
20°C	4.692	4.766	4.787
12°C	3.932	3.994	4.019
0°C	2.868	2.912	2.946
−2°C	2.701	2.745	2.786

Values are in S/m.

lack of permittivity measurements for natural seawater and the relatively imprecise and sparse permittivity data for aqueous ionic solutions.

One of our goals was to see whether or not there is a notable difference between the electric and dielectric properties of natural seawater, aqueous NaCl solutions, and "synthetic seawater." We prepared solutions of synthetic seawater which respected the proportions of each of the major ionic components of natural seawater. The permittivities of the synthetic seawater were then compared with those of natural seawater and an aqueous NaCl solution of the same salinity.

The recommended "recipe" for synthetic seawater, for use in chemical and biological studies, is that given by Grasshoff [1976]. It is as follows:

Step 1 is to dissolve in 500 mL of distilled water

Substance	Mass, g
NaCl	23.9
Na_2SO_4	4.0
KCL	0.7
$NaHCO_3$	0.2
KBr	0.1
H_3BO_3	0.03
NaF	0.003

Step 2 is to dissolve in 455 mL of distilled water

Substance	Mass, g
$MgCl_2,6H_2O$	10.8
$CaCl_2,2H_2O$	1.5

Step 3 is to mix the two solutions.

The salinity of the resulting mixture is 35‰. The results of the conductivity measurements for the three types of samples are in Table 5.

The conductivity of synthetic seawater is systematically higher than that of natural seawater. The mean percentage difference is about 1.5% at all temperatures. This is rather close to the experimental uncer-

tainty of the conductance meter which we used. This apparatus has to be calibrated; the calibration is accurate to 1%, and any error will give a systematic error in the measured result. This alone could produce a difference of 1%. Our conclusion is that to within the limits of our experimental technique, there is no difference between the conductivity of natural seawater and synthetic seawater over the temperature range −2°–30°C.

The conductivity of the aqueous NaCl solution is significantly higher than that of natural seawater at all temperatures. The difference varies between 2% and 3%. This is larger than the experimental uncertainty.

We conclude that the conductivity of an aqueous NaCl solution is between 2% and 3% higher than the conductivity of a natural seawater sample with the same salinity. This observation corroborates the work of Weyl [1964] and Ho and Hall [1973], who found a similar difference.

The permittivity measurements were in the frequency range 3–20 GHz and over the temperature range −2°–30°C in 1° steps. At all frequencies and temperatures the difference between natural and artificial seawater was within the 1% experimental uncertainty of our measuring system. We conclude that natural seawater and synthetic seawater have the same permittivity over these temperature and frequency ranges. There was a difference between natural seawater and the aqueous NaCl solution. The difference was maximum at 3 GHz and in the temperature range 0°–5°C, as can be seen in Figure 3. The difference in the permittivities was still significant up to about 10 GHz and rapidly drops to within the experimental uncertainty for higher frequencies.

As a conclusion to this section, for conductivity measurements and permittivity measurements in the frequency range 3–20 GHz and in the temperature range −2°–30°C, with a claimed experimental precision of about 1%, we found that (1) there is no significant difference between natural seawater and synthetic seawater made using the above standard recipe and (2) there is a significant difference in the conductivity and permittivity between natural seawater and an aqueous NaCl solution of the same salinity.

In view of these observations we suggest that any future measurements of the permittivity of seawater can be carried out using synthetic seawater made with the above recipe. This obviously reduces the cost and difficulty of obtaining natural seawater from remote areas. However, if it is ever required to obtain more precise permittivity measurements for seawater, espe-
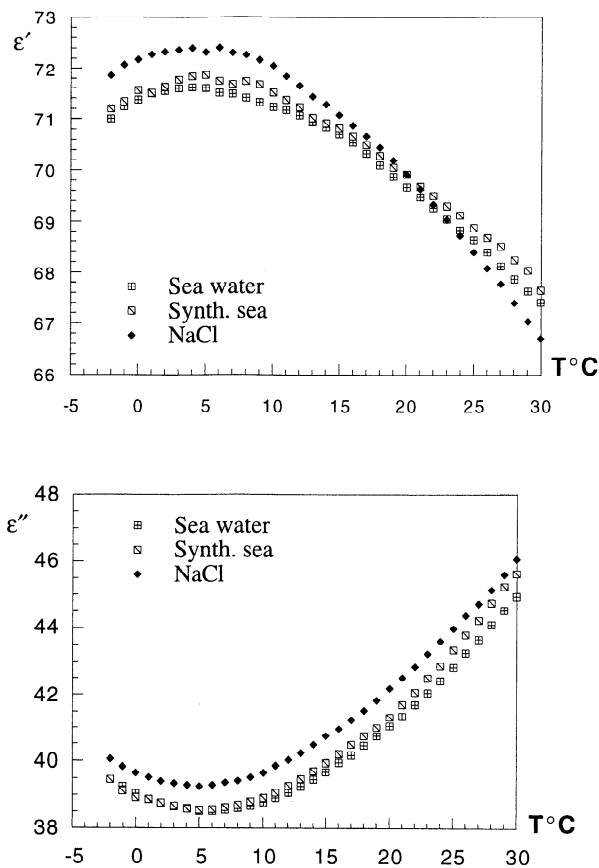
Figure 3. Comparison between the permittivities of natural seawater, synthetic seawater, and an NaCl solution, at 3 GHz, all with a salinity of 35‰.

cially for frequencies less than 3 GHz, then it will be necessary to redo a careful comparison between the synthetic seawater and the natural seawater samples.

6. Conclusion

We have shown that the permittivity $\varepsilon(\nu, t, S)$, of seawater can be calculated, to within 1%, by a simple Debye model for the parameter ranges $3 \leq \nu \leq 20$ GHz, $20‰ \leq S \leq 40‰$, and $-2° \leq t \leq 30°C$ and to within 3% over the extended frequency range $20 \leq \nu \leq 40$ GHz.

Our measurements at 89 GHz show that this model cannot be extrapolated to higher frequencies with an acceptable accuracy. However, in order to correctly exploit radar and radiometer data, it is essential to have precise permittivity measurements of natural seawater with an accuracy of better than 5% in the frequency range 40–100 GHz and in the temperature

range $-2°$–30°C in 1° steps in order to construct a more reliable model. Such measurements are in progress, and we shall report upon this work later.

We have also shown, on the one hand, that for frequencies between 3 and 10 GHz, there is a significant difference between the permittivities of natural seawater and an aqueous NaCl solution of the same salinity and, on the other hand, there is no significant difference between the permittivities of natural and synthetic seawater for frequencies greater than 3 GHz. This means that one does not have to go to the considerable trouble of collecting actual seawater samples for permittivity studies greater than 3 GHz. However, if it is ever necessary to have data which are more precise than our 1% experimental uncertainty or for frequencies less than 3 GHz, one should reconsider the comparison.

References

Aggarwal, S. K., and R. H. Johnston, Equations for complex relative permittivity of saline water, *IETE Tech. Rev. India*, 5(8), 317–320, 1988.

Barthel, J., F. Schmithals, and H. Behret, Untersuchungen zur Dispersion der komplexen Dielektrizitätskonstante wäbriger und nichtwäbriger Elektrolytlösungen, *Z. Phys. Chem. Neue Folge*, Bd71, 115–131, 1970.

Barthel, J., K. Buchhuber, R. Buchner, and H. Hetzenauer, Dielectric spectra of some common solvents: Water and lower alcohols, *Chem. Phys. Lett.*, 165, 369–373, 1990.

Barthel, J., K. Bachhuber, R. Buchner, H. Hetzenauer, and M. Kleebauer, A computer controlled system of transmission lines for the determination of the complex permittivity of lossy liquids between 8.5 and 90 GHz, *Ber. Bunsen Ges. Phys. Chem.*, 95(8), 583–588, 1991.

Barthel, J., K. Bachhuber, R. Buchner, and H. Hetzenauer, Dielectric relaxation of aqueous electrolyte solutions, *Ber. Bunsen Ges. Phys. Chem.*, 96(8), 988–997, 1992.

Blue, M. D., Permittivity of ice and water at millimeter wavelengths, *J. Geophys. Res.*, 85(C2), 1101–1106, 1980.

Buchner, R., G. T. Heffer, and J. Barthel, Dielectric relaxation of aqueous NaF and KF solutions, *J. Chem. Soc. Faraday Trans.*, 90, 2475–2479, 1994.

Cooper, R., The electrical properties of salt-water solutions over the frequency range 1–4000 Mc/s, *J. Inst. Electr. Eng. Tokyo*, 93(22), part III, 69–75, 1946.

Ellison, W. J., G. Delbos, L. Eymard, C. Guillou, and C. Prigent, The study and measurement of the dielectric properties of sea water: Interim report, ESTEC/ESA contract 11197/94/NL/CN, 1995.

Ellison, W. J., A. Balana, G. Delbos, K. Lamkaouchi, L. Eymard, C. Guillou, and C. Prigent, Study and measurement of the dielectric properties of sea water: Final Report, ESTEC/ESA contract 11197/94/NL/CN, 1996a.

Ellison, W. J., K. Lamkaouchi, and J. M. Moreau, Water: A dielectric reference, *J. Mol. Liq.*, 68, 171–279, 1996b.

Grant, E. H., and R. J. Sheppard, Dielectric relaxation in water in the neighborhood of 4°C, *J. Chem. Phys.*, 60, 1792–1796, 1974.

Grasshoff, K., *Methods of Seawater Analysis*, p. 317, Springer-Verlag, New York, 1976.

Guillou, C., W. J. Ellison, L. Eymard, K. Lamkaouchi, C. Prigent, G. Delbos, A. Balana, and S. A. Boukabara, Impact of new permittivity measurements on sea surface emissivity modeling in microwaves, *Radio Sci.*, this issue.

Haggis, G. H., J. B. Hasted, and T. J. Buchanan, The dielectric properties of water in solutions, *J. Chem. Phys.*, 20, 1452–1464, 1952.

Han, K. F., C. M. Butler, L. C. Shen, H. Y. He, and M. A. Harris, High frequency, complex dielectric permittivity of saline solution at elevated temperatures, *IEEE Trans. Geosci. Remote Sens.*, 29(1), 48–56, 1991.

Hasted, J. B., and S. H. M. El Sabeh, The dielectric properties of water in solutions, *Trans. Faraday Soc.*, 49, 1003–1011, 1953.

Hasted, J. B., D. M. Ritson, and C. H. Collie, Dielectric properties of aqueous ionic solutions, *J. Chem. Phys.*, 16, 1–21, 1948.

Ho, W., and W. F. Hall, Measurements of the dielectric properties of seawater and NaCl solutions at 2.65 GHz, *J. Geophys. Res.*, 78(27), 6301–6315, 1973.

Ho, W., A. W. Love, and M. J. Van Melle, Measurements of the dielectric properties of sea water at 1.43 GHz, *NASA Contract. Rep. CR-2458*, 1974.

Johri, G., M. Johri, and J. Roberts, Dielectric response of select ionic solutions using a loaded microwave cavity operating near 9 GHz, 21 GHz and 29 GHz as a probe, *J. Microwave Power Electromagn. Energy*, 26(2), 82–89, 1991.

Kaatze, U., Complex permittivity of water as function of frequency and temperature, *J. Chem. Eng. Data*, 34, 371–374, 1989.

Klein, L. A., and C. T. Swift, An improved model for the dielectric constant of sea water at microwave frequencies, *IEEE Trans. Antennas Propag.*, AP25(1), 104–111, 1977.

Kumar, A., Complex permittivity and microwave heating of pure water, tap water and salt solution, *Int. J. Electron.*, 17(6), 531–536, 1979.

Lamkaouchi, K., A. Balana, G. Delbos, and W. J. Ellison, Permittivity measurements of lossy liquids in the range 26–110 GHz, *IEEE Trans. Instrum. Meas.*, in press, 1997.

Lane, J., and J. Saxton, Dielectric dispersion in pure polar liquids at very high radio frequencies, III, The effects of electrolytes in solution, *Proc. R. Soc. London A*, 213, 531–545, 1952.

Liebe, H. J., G. A. Hufford, and T. Manabe, A model for the complex permittivity of water at frequencies below 1 THz, *Int. J. Infrared Millimeter Waves*, 12(7), 659–675, 1991.

McAvoy, J. G., and H. A. Buckmaster, The 9 GHz complex permittivity of dilute aqueous KCl solutions at 297 K, *J. Phys. Appl. Phys.*, 17, 2081–2085, 1984.

Richards, M. G. M., and R. J. Sheppard, A precision waveguide system for the measurement of complex permittivity of lossy liquids and solid tissues in the frequency range 20–90 GHz, II, The liquid system for 90 GHz; high-frequency cell design, *Meas. Sci. Technol.*, 2, 663–667, 1991.

Riley, J. P., and G. Skirrow, *Chemical Oceanography*, Academic, San Diego, Calif., 1965.

Saxton, J., and J. Lane, Electrical properties of sea water, *Wireless Eng.*, 29, 269–275, 1952.

Stogryn, A., Equations for calculating the dielectric constant of saline water, *IEEE Trans. Microwave Theory Tech.*, 19, 733–736, 1971.

Weiss, E., E. Gerdes, and H. J. Hoffmann, Messungen der Komplexen Dielektrizitäts-konstanten von Wasser und wäbrigen KCl-Lösungen bei 10 und 20 cm. Wellenlänge, *Z. Phys. Chem. Leipzig*, 228, 51–64, 1965.

Weyl, P., On the change in electrical conductance of sea water with temperature, *Limnol. Oceanogr.*, 9, 75–78, 1964.

Winsor, P., and R. H. Cole, Dielectric behaviour of aqueous NaCl solutions, *J. Phys. Chem.*, 89, 3775–3776, 1985.

A. Balana, G. Delbos, and W. Ellison, Laboratoire de Physique des Interactions Ondes-Matière, E.N.S.C.P.B., Université Bordeaux 1, 33402 Talence, France. (e-mail: gdelbos@piom.u-bordeaux.fr; w.ellison@piom.u-bordeaux.fr)

L. Eymard and C. Guillou, Centre d'étude des Environnements Terrestre et Planétaire, Centre Universitaire, 10-12 avenue de l'Europe, 78140 Vélizy, France. (e-mail: laurence.eymard@cetp.ipsl.fr; guillouc@cetp.ipsl.fr)

K. Lamkaouchi, Equipe de Spectronomie, Département de Physique, Faculté des Sciences, B. P. 4010, Meknès, Morocco.

C. Prigent, Goddard Institute for Space Studies, 2880 Broadway, New York, NY 10025.