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Broadband Electrical Response of Organic Contaminants and Contaminant/Soil Mixtures

by John O. Curtis

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Prepared for Laboratory Discretionary Research
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Final report

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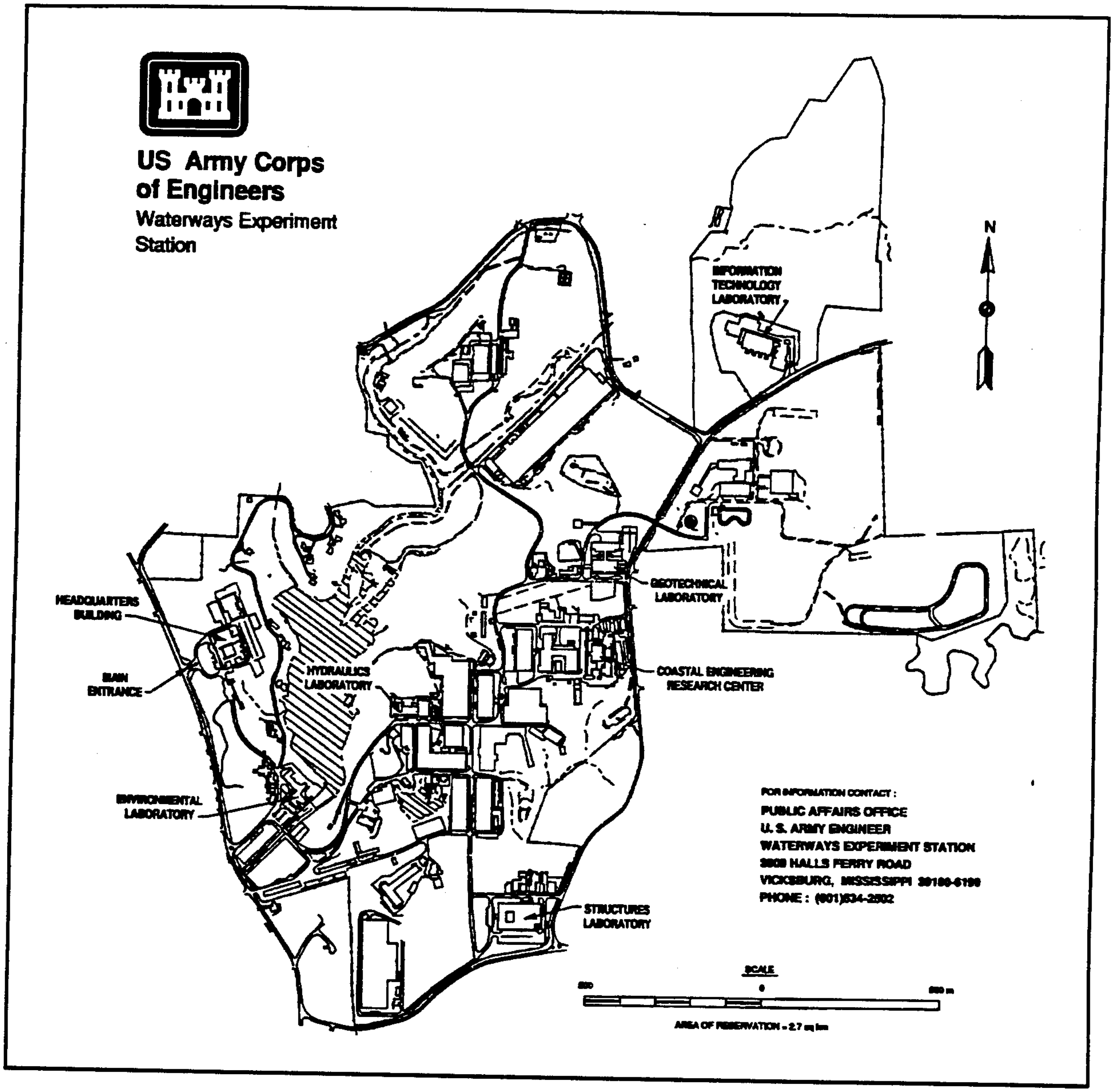

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Preface

The report herein documents efforts at the U.S. Army Engineer Waterways Experiment Station (WES), made during the 1993 and 1994 fiscal years, to explore the fundamental electrical properties of organic contaminants and contaminant/soil mixtures. Financial support for these studies came from the WES Laboratory Discretionary Research and Development Program, a basic research program managed by the WES Technical Director.

All of the work reported herein was conducted by Dr. John O. Curtis, a researcher within the Environmental Sensing Branch (ESB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES. This project was conducted under the direct supervision of Dr. Ernesto Cespedes, Chief, ESB, and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard.

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1 Background and Problem Statement

Driving Force—Environmental Cleanup

Soil and groundwater contamination is a problem that can no longer be ignored or willfully passed on to the next generation. A growing population confined to a finite land area has to become a better steward of its environment. If a major effort is not made now to limit the dumping of wastes into the atmosphere, water, and soil, the problems faced by succeeding generations may be insurmountable.

Identifying currently polluted terrain, quantifying the extent of its pollution, and taking action to begin the process of reversing the damage being done to the soil and groundwater is imperative. The number of hazardous waste sites in this country has been estimated at more than 100,000, of which as many as 75,000 may be considered serious enough for Superfund support (Abelson 1992).

One often thinks of radioactive substances and heavy metals as being the most important pollution generators. However, huge quantities of organic solvents have also been recklessly dumped into the ground and are working their way into the groundwater. In fact, Abelson also points out that organic solvents could present the largest cost factor in the remediation of Department of Energy sites.

The estimated cost of cleaning up existing hazardous waste sites is astronomical, with the projected cost of a "best job" effort being more than one trillion dollars. To make certain that environmental cleanup dollars are being spent as efficiently as possible, engineers and scientists must develop relatively low-cost, effective methods for detection of and characterization of subsurface contamination. Conventional sampling and monitoring technology is slow and costly.

Within the last decade, engineers and scientists have begun to explore the use of geophysical methods as a more efficient and cost-effective means of characterizing subsurface conditions (Walther, Pitchford, and Olhoeft 1986).

Among these methods are ground-penetrating radar for near-surface applications, high-frequency electromagnetic sounders for deeper studies, and airborne low-frequency sounders for even greater depths of penetration (Campbell et al. 1990). Another approach to efficiently characterizing suspected contamination sites is that being taken by the U.S. Army. The Army produced a truck-mounted penetrometer that is capable of housing numerous in situ sensors for the detection and identification of particular contaminants in addition to the geophysical characterization of the soil layers (Lee et al. 1993).

The goal of the research effort reported herein is to explore the potential for developing a sensor that makes use of the unique electromagnetic signature of contaminated soils and soil/water mixtures and that could be part of the sensor suite in a probe such as the penetrometer referenced above. The specific region of interest includes the microwave portion of the electromagnetic spectrum (frequencies ranging from 50 MHz to more than 20 GHz; wavelengths ranging from less than 1.5 cm to 6 m), where the oscillating electric fields interact with the permanent electric dipole moments of both water molecules and many organic contaminants.

Previous Research

Material property investigations

The most thorough collection of contaminant dielectric property measurements in the microwave range that has been reported in the literature is that found in a 1958 National Bureau of Standards publication (Buckley and Maryott 1958); however, the data reported therein were limited to frequencies less than 50 MHz. Other efforts have been made to collect electrical property data for hazardous materials as part of a broader database of useful information (Lucius et al. 1992). However these data are normally for single frequencies and may not be in the range of interest for a particular application. Some researchers have used published low-frequency data in support of a particular field experiment or in support of certain electrical response model studies (to be discussed in the next sections).

Some researchers have conducted intensive microwave property studies of selected chemicals for the purpose of better understanding the structure of those particular molecules (Kay, Vidulich, and Berberian 1967; Berberian 1983; Cole et al. 1989; Su, Liu, and Quade 1993). An array of experimental apparatuses are used in this research, including time-domain reflectance cells (Berberian and Cole 1969; Cole 1976; Berberian and Cole 1992), bridge circuit devices (Cole 1983), and frequency domain absorption cells (Su 1994).

Model studies

A number of very interesting models for predicting physical properties of soils from electrical property measurements have been developed. While this may not seem to be related to a study of the electrical properties of contaminants, some of the models are, in fact, just attempts to deal with mixtures of substances whose dielectric properties differ. In that sense, a particular contaminant can be thought of as one of those components.

Early modeling efforts in this country began with measurements of the dielectric response of various clay minerals saturated with either pure water or other well-defined pore fluids and interpretation of those responses in terms of simple electrical analogues (Mitchell and Arulananadan 1968; Smith and Arulanandan 1981). Also for media saturated with water, the anisotropic electrical response of soils has been related to soil porosity through a model in which the soil particles are assumed to be spheroids imbedded in a fluid matrix (Arulanandan 1991; Thevananyagam 1993). Another effort attempts to relate the difference in electrical permittivity of soils measured at two different frequencies (and called "dielectric dispersion") to the type of clay minerals present and pore fluid concentration (Arunlanandan, Yogachandran, and Rashidi 1994). A recent study by this author also relates soil-water-air mixture dielectric responses to both fairly sophisticated electrical analogues and to a fractal model of soil structure (Curtis 1993b). Finally, one reported study attacks the problem of soil-contaminant electrical responses with an inclusion-based model that examines pore-scale fluid distributions (Endres and Redman 1993).

Field measurements

Descriptions of field measurements of subsurface contaminants have been reported in the literature during the last decade. These studies were performed to either assess the current state of contamination (Olhoeft 1986; Smith 1992) or to evaluate various geophysical techniques for detecting the presence of certain contaminants in a controlled environment (DeRyck, Redman and Annan 1993; Greenhouse et al. 1993; Hanson, Tweeton, and Friedel 1993).

Olhoeft provided an overview of a number of field measurement programs at either known or suspected contaminated sites including ones in Nevada, Louisiana, Minnesota, and Florida (Olhoeft 1986). Geophysical techniques used included electromagnetic induction, DC resistivity, complex resistivity (measurements of both amplitude and phase), and ground-penetrating radar. Subsurface organic contaminant plumes are detectable in clayey soils using the complex resistivity technique because of the disruption of normal surface conduction processes within the clay structures. On the other hand, inorganic plumes tend to generate conductivity anomalies measurable by the electromagnetic and DC techniques. These observations have been confirmed in later studies (Olhoeft and King 1991). Radar measurements were found to be somewhat useful in sandy soils where the presence of the contaminant generates a dielectric property discontinuity.

Helicopter-borne electromagnetic induction techniques have been used to map concentrations of subsurface brine (Smith 1992). Some of the useful observations made from this study were that the technique can work well if the uncontaminated background resistivities are high, that the technique requires some fairly sophisticated modeling and data processing, and that cultural anomalies present little difficulty (which would have happened with traditional resistivity soundings).

A thorough and controlled experiment on the use of geophysical methods to detect the time-dependent behavior of a dense nonaqueous phase liquid, or DNAPL (in this case, perchloroethylene (PCE)), injected into a sandy aquifer was conducted in 1991 at the Canadian Forces Base Borden (Greenhouse et al. 1993). Equipment used included devices to measure electrical resistivity, dielectric permittivity, neutron logs, gamma logs, and ground-penetrating radar. In this very specialized environment, all of the techniques provided an indication of the movement of the DNAPL through the aquifer. The dielectric contrast accounted for the ability of the ground-penetrating radar to "see" the DNAPL.

A similar experiment was conducted later at Borden (DeRyck, Redman, and Annan 1993) in which the contaminant of interest was a light nonaqueous phase liquid, or LNAPL (in this case, kerosene). Once again, in a very controlled environment, the geophysical methods were sensitive to the material property contrast created by the displacement of the water in the capillary zone and the filling of the pore spaces in the unsaturated zone by the LNAPL.

One other field experiment on note was conducted in Arizona in 1990 that involved the evaluation of several electromagnetic techniques for locating deep subsurface conductive fluids such as brine (Hanson, Tweeton, and Friedel 1993). Six different devices were used to map a conductive solution injected 160 m below the ground surface. As the application here is within the mining industry, and the spatial resolution of such devices is extremely poor, all that needs to be noted here is that several of the devices were able to detect the changes brought about by the injection of the fluid.

New probe designs

While the field trials referenced above can be effective in providing indications of subsurface contamination, they do not possess the spatial resolution to accurately map subsurface conditions. What is needed is a large number of point measurements taken throughout a volume of earth that can be processed to produce very useful three-dimensional pictures of contaminant plumes. Standard boring and sampling techniques are far too expensive for this task. Attention is now being focused on cone penetrometer devices that can probe huge volumes of earth relatively cheaply and quickly (nonrocky soils), in which a whole suite of characterization sensors can be installed into the penetrometer. Data can then be collected in near real-time as the probe is pushed into the soil. Obviously, for this study, the emphasis is on electromagnetic devices. Some prototypes do exist.

Arulanandan and Arulanandan (1986) have developed a prototype sensor for measuring the dielectric permittivity and conductivity of soils at frequencies up to about 50 MHz. Their sensor could be installed in a penetrometer. Some work has been done to relate such measurements to the presence and concentration of a particular contaminant in rather specialized soils.

Another scheme for conducting point measurements of contaminants in soils is that of Yong and Hoppe (1989). Their prototype apparatus consists of an electromagnetic pulse generator and a length of coaxial line that is terminated in the soil by an extended center conductor. Also part of the apparatus is a detector capable of measuring the time-domain reflectance of the signal from the contaminated soil. Fast Fourier Transform techniques are applied to the recorded data to examine its frequency-domain behavior. The authors have published data on measurements of soils both saturated and less than saturated with several liquids and demonstrated that their apparatus has the potential for being a contaminant detector.

Apparently, numerous examples exist of the application of electrical resistivity devices to the penetrometer geometry. Campanella and Weemees (1990) reported on a 1,000-Hz resistivity cone coupled with several other geophysical sensors. While they did not publish data on the use of their device to profile a known contaminant plume, it was used to profile a nondistinct freshwater to saltwater transition. They did reference a recent study of soils contaminated with aromatic hydrocarbons that exhibited very large resistivity values in which the penetrometer sensor successfully mapped the contaminant plume.

The U.S. Army has also developed and reported on a DC resistivity cone developed for its Site Characterization and Analysis Penetrometer System, or SCAPS (Koester et al. 1993). The most interesting observation made in one particular study was that, even though chlorinated solvents might be highly resistive, if they exist above the water table, they may not be easily distinguishable from the highly resistive dry soils.

One final example of possible contaminant sensor technology is another prototype being studied by the U.S. Army (Everett and Curtis, In Preparation). It is similar in concept to the probe of Yong and Hoppe (1989) except that it operates at a fixed frequency of 60 MHz and measures the complex dielectric constant of the soil/moisture/air mixture adjacent to the coaxial termination at that single frequency. This probe was developed to demonstrate the feasibility of using a microwave reflectometer to accurately measure subsurface dielectric properties. If sufficient laboratory data can be collected to develop empirical relationships of complex dielectric properties of a broad range of soils and contaminants, then it may be possible to use this probe architecture in a penetrometer-mounted sensor to help evaluate the extent of subsurface plumes.

Focus of This Research

Electrical and electromagnetic geophysical methods can be very sensitive indicators of change caused by the movement (or dissipation) of contaminant plumes through soils (Olhoeft 1992). Although such techniques will probably never be useful for validating regulatory levels of contaminants (parts per million or less), research into the properties of contaminants and soil/contaminant mixtures should continue and should be aimed at improving the successful applications of geophysical methods to the detection of contaminants in our environment.

In this spirit, the focus of research reported herein is to begin to examine the electrical properties of contaminants and contaminant/soil/water mixtures over a broad range of frequencies in the microwave portion of the spectrum. The intent of this effort is to determine whether or not unique electromagnetic signatures exist and whether or not these signatures can be taken advantage of to develop a sensor that could be used to help characterize contaminated soils.

There are at least three types of questions that can be asked to help direct a basic research program such as the effort reported here. One type involves the predictability of dielectric properties. Another addresses issues of masking effects; i.e., the interactions of mixture constituents. And finally, the last set of questions might deal with looking forward to applying this new knowledge to real sensor development. Specifically, one might pose these questions in the following ways:

a. Can the relative dielectric response of pure contaminants be predicted from their physical properties? For example, is there a predictable trend in any resonant frequencies (if they exist) that is tied to the molecular weight of the chemical or to the magnitude of its permanent dipole moment (if it exists)?

b. How do other mixture constituents affect the dielectric response of pure contaminants? Does a pure water/contaminant mixture obey a particular mixing law? Do pure contaminants in clean soils follow the same law? Does a mixture of water, soil, and contaminant follow the same mixing law?

c. If you were going to design a hypothetical electromagnetic sensor for detecting subsurface contaminants, how would it work? Can one predict its sensitivity based on the measurements reported in this and other studies?

2 Experimental Procedure and Material Descriptions

Questions of predictability of response of pure contaminants as well as contaminant/soil mixtures cannot be answered without carefully controlled experiments. Some data do exist and are referenced in the literature. However, these reports often deal with a single contaminant, or a limited range of frequencies, or with soils that are not well characterized, or often fail to include careful volume fraction measurements. The strengths of the experiments reported here are exactly the weaknesses reported elsewhere: several pure contaminants measured over a broad range of frequencies with the same experimental procedure and careful volume fraction measurements.

Experimental Apparatus

The apparatus used to collect complex dielectric constant data is a modification of an earlier system developed at the U.S. Army Engineer Waterways Experiment Station (WES) (Curtis 1993a) and is shown in block diagram form in Figure 1. The system is built around a Hewlett Packard 8510C Vector Network Analyzer, which controls a synthesized source and an S-parameter test set. Specialized flexible cables connect the test set to unique coaxial sample holders that were developed at WES. The holders (shown in Figure 2) were machined from brass stock and have a cross section of 7.5 by 7.5 mm. For previous studies, sample holders were manufactured with both 15- and 100-mm-length cavities to ensure that valid data could be collected at the extremes of the frequency sweep for both low-loss and high-loss materials. Because of the relatively low losses associated with the materials of interest in this research, the 100-mm cavities were the only ones used for this study. Connection to the test set cables is made through SMA connectors on the ends of the sample holders and a pair of 3.5-mm adapters.

Control of the network analyzer measurement system, creation of raw data files, and plotting of complex dielectric constants are accomplished by an HP-9000-362 instrument controller. Further processing and display of data took place on an off-line PC using the SAS software system (SAS Institute 1988).

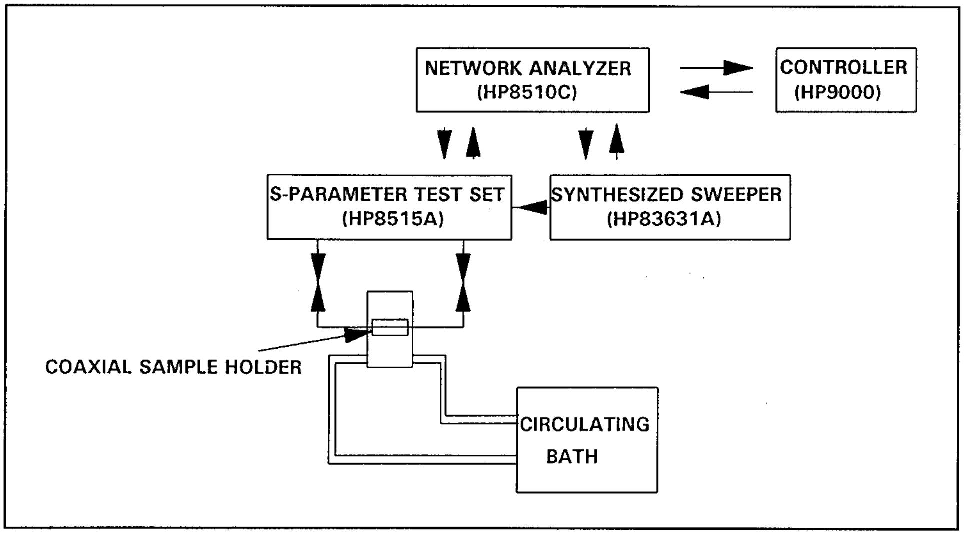


Figure 1. Dielectric property measurement apparatus block diagram

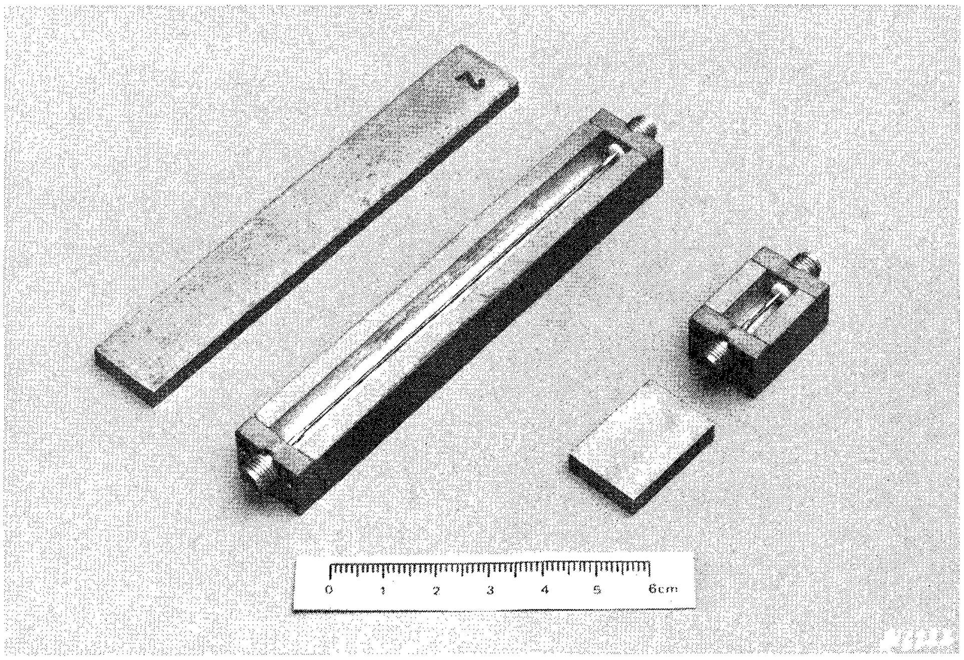


Figure 2. Brass square cross-section coaxial sample holders

Governing Equation

The synthesized source has the capability of generating signals that span a 45-MHz to 26.5-GHz range. Complex reflection and transmission coefficients (S_{11} and S_{21}, respectively) are measured by the test set. Assuming plane wave behavior within nonmagnetic samples, one can show that the relative complex dielectric constant (here written as ϵ) can be calculated from the following governing equation (Curtis 1993a):

$$\cos\left[\omega d \frac{\sqrt{\epsilon}}{c}\right] = \frac{1 + (S_{21})^2 - (S_{11})^2}{2S_{21}} \tag{1}$$

where

d = length of the sample

The right-hand side of this equation is a vector in complex space that rotates about the origin as frequency changes. As it crosses the real axis, both on the positive side and on the negative side, it passes through or near branch cuts for the inverse cosine function (Abramowitz and Stegun 1972), leading to instabilities in the calculation of the argument on the left. As will be seen later, plots of the real part of the complex dielectric constant against frequency take on the characteristics of anomalous dispersion (Jackson 1975) at these points where the complex vector approaches the real axis.

A physical description of what is happening within the test sample at these points of instability may best be seen when one attempts to measure the response of the empty sample holder; i.e., a measurement of the complex dielectric constant of air. The relative constant for air has a real part equal to unity and an imaginary part equal to zero. One can then rewrite the argument of the cosine function in the governing equation as a function of wavelength and sample cavity length

$$\frac{\omega d\sqrt{\epsilon}}{c} = \pi\left[\frac{d}{\lambda/2}\right]$$

At the same time, experimental results show that the complex vector from the right-hand side of Equation 1 rotates through the real axis on both sides with a value of nearly unity. Now the inverse cosine function evaluated at unity is $2k\pi$, and the function evaluated at negative unity is $(\pi + 2k\pi)$. In other words, every integer multiple of π is accounted for. Then the argument of the cosine function can be set equal to an integer multiple, n, of π, leading to the conclusion that, as the complex vector crosses the real axis,

$$d = n(\lambda/2)$$

Therefore, the instability in the calculation of complex dielectric properties takes place whenever the sample contains an integer multiple of half wavelengths.

Calibration Procedure

Prior to collecting data on moist soil samples, a full 2-port calibration was performed using an HP85052B, 3.5-mm Calibration Kit. Under normal conditions, each calibration would hold for several hours before instrumentation drift would force the system out of acceptable limits. The limits were defined by the amplitude and phase measurements made when the two S-parameter test cables were directly connected. A calibration was considered to be valid when the amplitude did not vary more than 0.1 db over the entire range of frequencies, and when the phase did not vary more than 1 deg over the frequency range.

As described elsewhere (Curtis 1993a), one other correction had to be made to the data, even after a successful calibration, before correct values of the dielectric constant could be computed. Because of the requirements for adapters between the sample holder SMA connectors and the S-parameter test set cables and because of the existence of the SMA connectors, themselves, an electrical delay had to be added to each parameter (S_{11} and S_{21}) to account for the additional electrical path length between the calibration planes at the ends of the cables and the surface of the sample. For these measurements, the necessary electrical delay for each parameter was found to be 270 picoseconds.

One final adjustment to the model for calculating complex dielectric constants involves a slight decrease in the sample length used in the inversion of Equation 1. Instead of a sample length of 100 mm, a length of 97 mm was used to provide a reasonable tradeoff between the measured response of two known quantities, air and pure water, and what those numbers are expected to be and to account for the observation that effective cavity length is not exactly 100 mm. This is due to the fact that the SMA connectors utilized in the end plates of the sample holders have dielectric sleeves around the center conductor that extend a short distance into the sample cavity. An analytical effort to model the true sample holder geometry and to predict an effective sample length is beyond the scope of this project.

Procedure Validation

An example of the results generated by this experimental procedure is shown in Figure 3. These data are for an empty 100-mm sample holder, thus representing a measurement of the complex dielectric constant for air. Note that the experimental results are very close to the theoretical results of a real part equal to unity and an imaginary part equal to zero. Note also the frequencies at which the calculation instability shows up as anomalous dispersions. Calculations verify that these unstable points occur at frequencies where an integer number of half wavelengths exist in the sample holder.

Figure 4 is another example of data collected by the laboratory system. In this case, the substance being measured is distilled, deionized water. Because

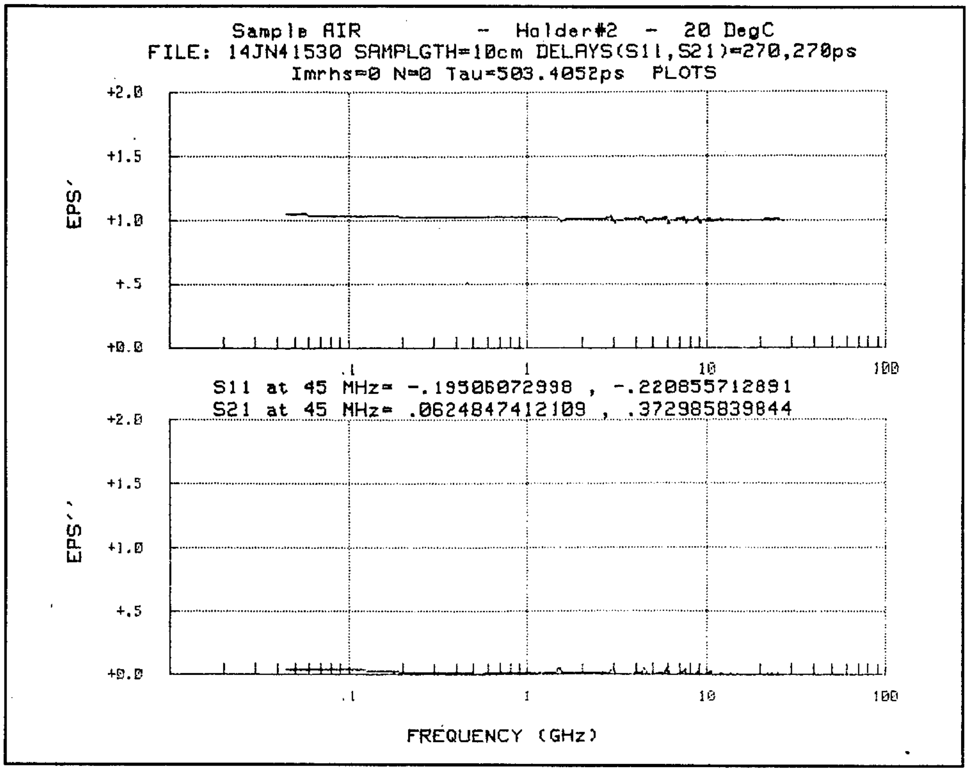


Figure 3. Complex dielectric constant for air, 100-mm holder

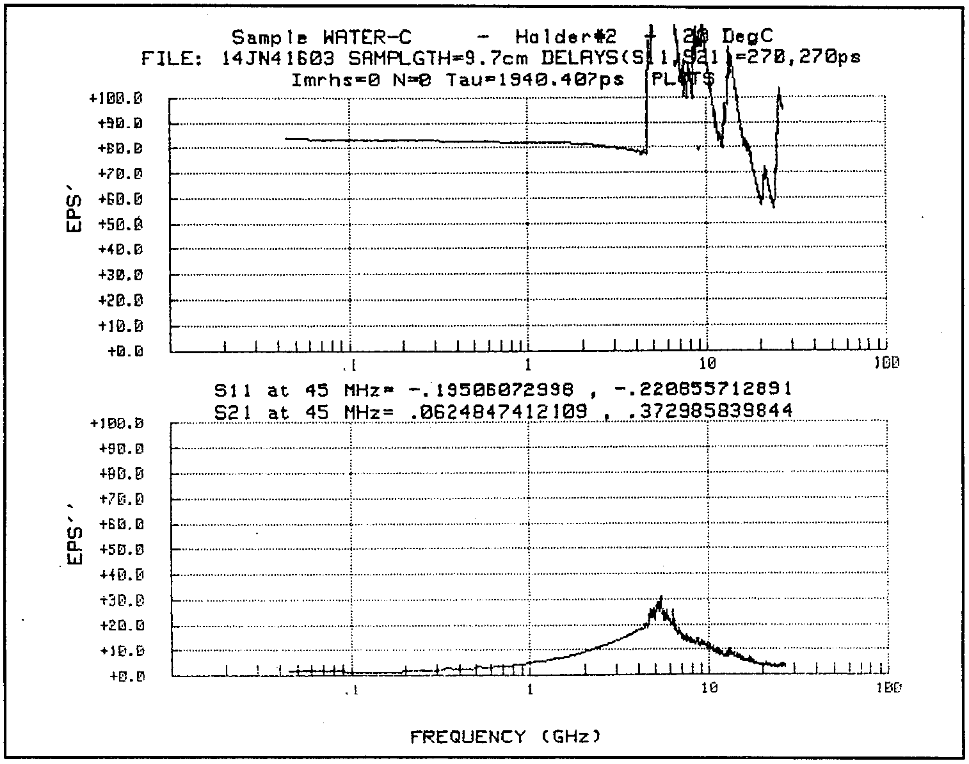


Figure 4. Complex dielectric constant for water, 100-mm holder

of the length of the sample holder and the high level of attenuation of water, a measurable signal was lost for frequencies higher than 4 GHz. Note that there are virtually no conductivity losses at low frequencies, further indication of the purity of the liquid.

Materials Investigated and Data Collection Procedures

Organic contaminants

The laboratory apparatus used to measure complex dielectric properties of contaminants and soil/contaminant mixtures and the laboratory space within which it is located placed some restrictions on the contaminants that could be safely studied. The first constraint was that the chemical had to be reasonably nonvolatile. If its vapor pressure was too high, an excessive amount of the contaminant would escape before the sample temperature reached equilibrium and a measurement of its dielectric properties could be made.

An extremely useful document for identifying significant contaminants and their physical properties, such as vapor pressure, was the U.S. Geological Survey report entitled "Properties and Hazards of 108 Selected Substances—1992 Edition" (Lucius et al. 1992). From a table of the 20 most frequently detected organic groundwater contaminants, a number of chemicals were selected for study whose vapor pressure at 20 °C is less than 3 kPa (about 0.5 psi). The selected contaminants also had to possess a nonzero electric dipole moment (so that they would react to an oscillating electric field and, hence, exhibit a complex dielectric constant). The chemicals chosen, including pure ethylene glycol that was readily available, are listed in Table 1 along with their physical and chemical properties that may prove useful in predicting their dielectric response.

Table 1
Characteristics of Selected Contaminants

Compound	Formula	Toxicity	Relative Mass	Boiling Point °C	Dipole Moment D[1]	Viscosity 20 °C mPa-s	Specific Gravity	Permittivity
Chlorobenzene	C_6H_5Cl	moderate	112.6	132	1.65	0.80	1.10	5.8
Dibutyl Phthalate	$C_{16}H_{22}O_4$	low	278.3	340	2.55	20.3	1.05	6.4
Dioctyl Phthalate	$C_{24}H_{38}O_4$	low	390.6	385	2.85	81.4	0.98	5.2
Ethylbenzene	C_8H_{10}	moderate	106.2	136	0.45	0.678	0.87	2.4
Ethylene Glycol	$C_2H_6O_2$	moderate	62.07	197	2.28	19.9	1.10	38
Phenol	C_6H_6O	high	94.1	182	1.50	12.4	1.06	10
Toluene	C_7H_8	moderate	92.14	110	0.36	0.590	0.87	2.4

[1] D stands for Debyes, which are equivalent to 3.336 × 10^{-30} coulomb-meters. The dipole moment for water is 1.85 Debyes.

Measurements of the dielectric response of these organic contaminants were made by simply filling the sample holder with liquid drawn from a pipette and placing it into the heat sink/source (Figure 5) where its temperature was brought to the desired value (usually 20 °C). Collection of complex reflection and transmission data and subsequent calculation of complex dielectric constants at any desired temperature was achieved by interactively executing the data controller code reported elsewhere (Curtis 1993b). The entire frequency range of 45 MHz to 26.5 GHz was divided into 800 steps. At each frequency step, the S_{11} and S_{21} data collected represent an average of 64 readings. After measurements are made at one temperature setting, a new sample temperature (if desired) is selected on the Caron circulating bath control panel, and another set of measurements is made once the new temperature is reached and equilibrium is allowed to be achieved. A separate data file is created for each sample holder and at each temperature. The measurement process for any one chemical at one temperature takes about 20 min (allowing for a reasonable amount of time for temperature equilibrium to be reached).

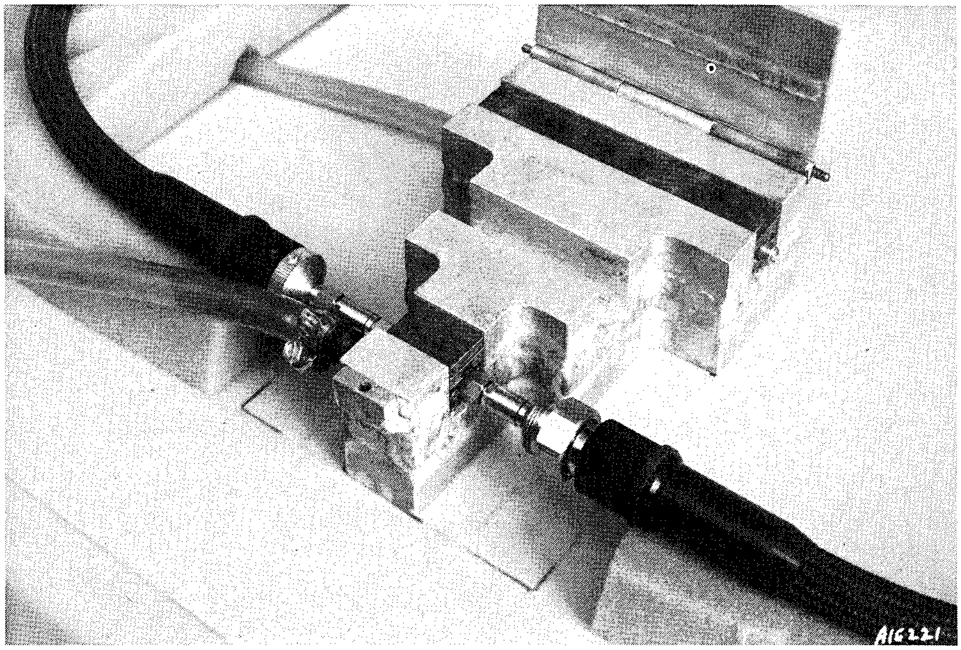
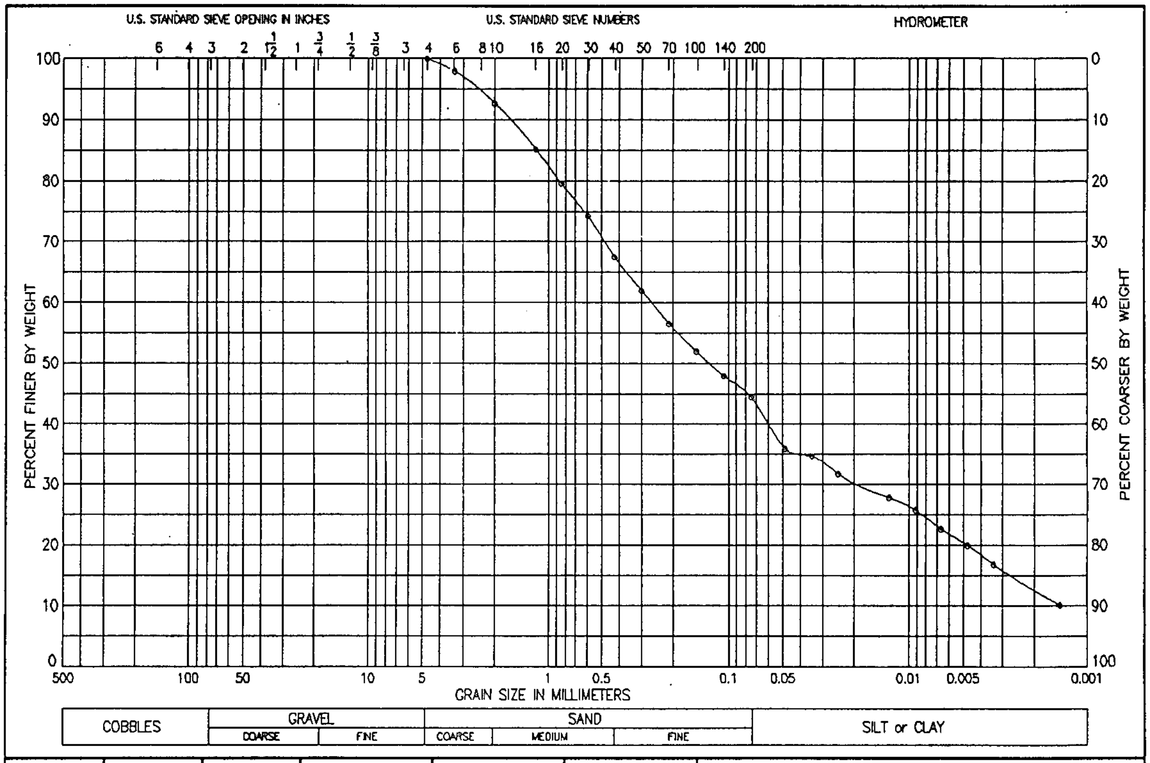


Figure 5. Sample holder placed in sink/source with cables attached

Soil

The soil used in this study was a well-graded clayey sand that was free of organic matter and had been processed for ease of handling (oven-dried, pulverized, and screened to remove large grains). Its grain-size distribution curve is shown on Figure 6. Table 2 is a summary of its physical and chemical properties taken from an earlier reference (Curtis, Weiss, and Everett, In Preparation).



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CLASSIFICATION
CLAYEY SAND (SC), DARK BROWN

PROJECT SOIL SAMPLES FOR CONTAMINANT STUDIES

BORING NO. SAMPLE NO. G

DEPTH/ELEV DATE 16 APR 93

GRADATION CURVE | LABORATORY USAE WES – STF/GL

Figure 6. Soil gradation curve

Table 2
Soil Properties

Description	Clayey Sand (SC), Dark Brown	Chemical Composition percent		Mineral Phases, percent	
Liquid Limit	38	SiO_2	75.4	Quartz	28
Plastic Limit	17	Al_2O_3	15.5	Smectite	64
Specific Gravity	2.66	MgO	0.6	Calcite	trace
Specific Surface	33.18 m^2/g	Na_2O	1.4	K-Feldspar	5
Average Sphericity	0.7	P_2O_5	0.1	Na-Plagioclase	3
Average Roundness	0.5	CaO	0.6	Mica	0
		K_2O	1.4	Kaolinite	trace
		Fe_2O_3	3.5	Dolomite	0
		TiO_2	0.5	Cristobalite	0
		MnO	0.0		

Soil/contaminant measurements were limited to the clayey sand and ethylene glycol because of the low vapor pressure of this chemical and its relatively strong dielectric response. The feeling was that this combination of materials would produce the most sensitive test of mixture theories. As will be shown in the next chapter, data were collected for soil/glycol mixtures and for a soil/glycol/water mixture.

The soil/glycol mixtures were studied by first filling the sample holder with dry soil and making a measurement over the entire range of frequencies. The mass of the soil and holder was recorded to allow for later determination of the dry soil density. Next, a small amount of glycol was dropped onto the soil in the holder, which displaced some of the air in the soil pore spaces. The mass of the mixture and holder was recorded to allow for the volumetric moisture level of the glycol to be later calculated. Following another network analyzer measurement sequence, more glycol was added and the procedure repeated until all of the data had been collected.

As for the soil/glycol/water measurement, approximately equal amounts of ethylene glycol and water were added to a quantity of soil and mixed in a glass dish. Specifically, ethylene glycol was added first, mixed with the soil, and the two were weighed. Distilled deionized water was then added, the combination of ingredients mixed again, and then weighed again. The dish was sealed in a plastic bag and allowed to cure for more than 2 hr before the mixture was "spooned" into the holder (Figure 7) and the measurements conducted.

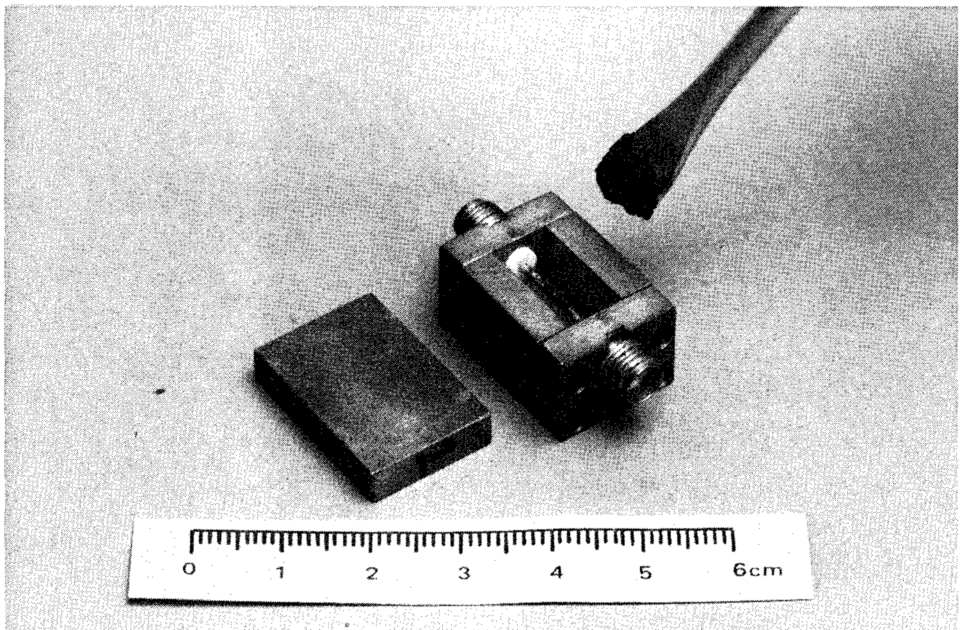


Figure 7. Filling a sample holder with soil/liquid mixture

3 Experimental Results

Test Matrix

A concise summary of the measurements conducted in this study is shown in Table 3. All of the pure contaminants identified in Table 1 were examined except for phenol. The decision not to test phenol was made because of its high degree of toxicity and the difficulty in safely handling this substance within the laboratory procedures described earlier. Data collected to help answer the questions about the response of mixtures were limited to those of the one well-graded clayey sand and mixtures of pure ethylene glycol or a combination of ethylene glycol and pure water. One additional measurement of pure glycol and pure water was also conducted to further address mixture questions.

Table 3
Matrix of Experiments

Substance or Mixture	10 °C	20 °C	30 °C	40 °C
Ethylene Glycol	X	X	X	X
Dibutyl Phthalate	X	X	X	X
Dioctyl Phthalate	X	X	X	X
Chlorobenzene	X	X	X	X
Toluene	X	X	X	X
Ethylbenzene	X	X	X	X
Dry Soil		X		
Soil + 14 percent Glycol (by volume)		X		
Soil + 25.9 percent Glycol		X		
Soil + 36 percent Glycol		X		
Soil + 20.0 percent Glycol + 23.4 percent Water		X		
48.5 percent Glycol + 51.5 percent Water (by volume)		X		

Fundamental Relationships for Data Presentation

As was discussed in Chapter 2, the measured complex reflection and transmission coefficients for any sample being tested can be used to calculate a complex dielectric constant using Equation 1. However, researchers who are dealing with the propagation of electromagnetic energy through media seldom use a common terminology for expressing the results of their studies. Some prefer complex dielectric constants as a description of material behavior. Others prefer to talk about electrical conductivity. Many speak in terms of a parameter called the loss tangent. And yet others prefer to focus on how the signal attenuates through the media.

The relationships that follow will be useful in interpreting the experimental results as will be discussed in a later chapter and, hopefully, provide enough ways to visualize the data to satisfy any interested reader. Supporting references include Jackson (1975), Stratton (1941), and Bohren and Huffman (1983).

For these derivations, plane harmonic wave propagation is assumed in a lossy, nonmagnetic, unbounded medium. Therefore, one may assume that the amplitude function for the plane wave looks like:

$$e^{i(kx - \omega t)}$$

where

i = symbol designating an imaginary quantity $= \sqrt{-1}$

$k = \beta + i\alpha = \omega N/c \qquad (2)$

= complex propagation constant

β = phase constant

α = amplitude attenuation factor

ω = radial frequency

N = complex index of refraction

c = velocity of light in a vacuum

x = a space coordinate

t = time

Furthermore,

$$N^2 = \epsilon = \epsilon' + i\epsilon'' \tag{3}$$

where, as stated earlier, ϵ is the relative complex dielectric constant, which, along with the electrical conductivity from Ohm's Law, represents the electrical properties of the medium. The interpretation of these properties as used in this study is that the conductivity, σ, accounts for current due to free charged particle motion, while the imaginary part of the complex dielectric constant, ϵ'', accounts for displacement current losses (those due to the electric polarization of the medium). When both conduction and displacement currents are considered, one finds two terms in Ampere's law for current flow that represent losses (or a shift in phase), one containing the electrical conductivity and one containing the imaginary part of the dielectric constant. While these two terms account for different loss mechanisms, most researchers use only one term or the other to identify losses, with many users preferring to deal with the concept of electrical conductivity. In SI units, the relationship between the two quantities is taken to be

$$\sigma = \epsilon'' \epsilon_0 \omega \tag{4}$$

where the units of conductivity are mhos/meter (or siemens/meter) and ϵ_0 is the permittivity of free space (8.85×10^{-12} farads/meter). However, in the development of the fundamental relationships used to interpret laboratory data, it was found more convenient to account for the dispersive properties of the medium completely by the complex dielectric constant (implicit in Equation 3). When electrical conductivity is desired, Equation 4 will be utilized.

Combining the square of Equation 2 with Equation 3 and equating real and imaginary components result in two algebraic equations that relate the amplitude attenuation factor and phase constant to the complex dielectric constant:

$$\beta^2 - \alpha^2 = \frac{\omega^2}{c^2}\epsilon'$$

and

$$\alpha\beta = \frac{\omega^2 \epsilon''}{2c^2}$$

Solving these equations for the amplitude attenuation factor and for the phase constant results in the following expressions:

$$\alpha = \frac{\omega}{c}\left[\frac{\epsilon'}{2}\left[\sqrt{1+\left[\frac{\epsilon''}{\epsilon'}\right]^2}-1\right]\right]^{1/2} \tag{5}$$

and

$$\beta = \frac{\omega}{c}\left[\frac{\epsilon'}{2}\left[\sqrt{1+\left[\frac{\epsilon''}{\epsilon'}\right]^2}+1\right]\right]^{1/2} \tag{6}$$

The ϵ''/ϵ' ratio is also referred to as the loss tangent. Some researchers prefer to work with the electrical conductivity (Equation 4) in place of the dielectric loss term.

Plane waves of constant phase (but not necessarily energy or signal) will propagate with a velocity

$$v = \frac{\omega}{\beta} = c\left[\frac{\epsilon'}{2}\left[\sqrt{1+\left[\frac{\epsilon''}{\epsilon'}\right]^2}+1\right]\right]^{-1/2} \tag{7}$$

The power intensity of the plane electromagnetic wave decreases exponentially with depth of penetration by the factor, $e^{-2\alpha x}$, or, in one unit of distance traveled, a decrease of $e^{-2\alpha}$. Power attenuation expressed in decibels per meter can then be written as:

$$PL = -8.6859\,\frac{\omega}{c}\left[\frac{\epsilon'}{2}\left[\sqrt{1+\left[\frac{\epsilon''}{\epsilon'}\right]^2}-1\right]\right]^{1/2} \tag{8}$$

Experimental Results

The results of reflection/transmission measurements on the materials identified in Table 3 are graphically presented on the pages that follow. Each figure contains two parameters plotted against the frequency of the source. Normalized phase velocity is just the phase velocity from Equation 7 divided by the speed of light in a vacuum.

Figures 8-13 represent the experimental results for the pure contaminants. Most of the data are well behaved. One exception is for chlorobenzene, where the sample resonance conditions discussed in Chapter 2 combine with high transmission signals (low losses) to produce exaggerated spikes in all of the loss-related terms. The other exceptions are for both toluene and ethylbenzene, where low losses result in only the real part of the dielectric constant and the normalized phase velocity being useful data. All of the loss-related terms should be ignored for these substances.

Figure 14 represents the experimental results for all of the mixtures identified in Table 3 for which data were collected at a temperature of 20 °C. Data labeled 0.0-, 14.0-, 25.9-, and 36.0-percent glycol are for the soil-glycol mixtures. The 48.5-percent data is for the glycol-water mixture, and 99.0 percent is a phony label for the soil-glycol-water mixture. Data labeled 100.0 percent is for pure ethylene glycol. All of these data are quite well-behaved except for 25.9-percent glycol-soil mixture that exhibits half-wavelength resonances at high frequencies.

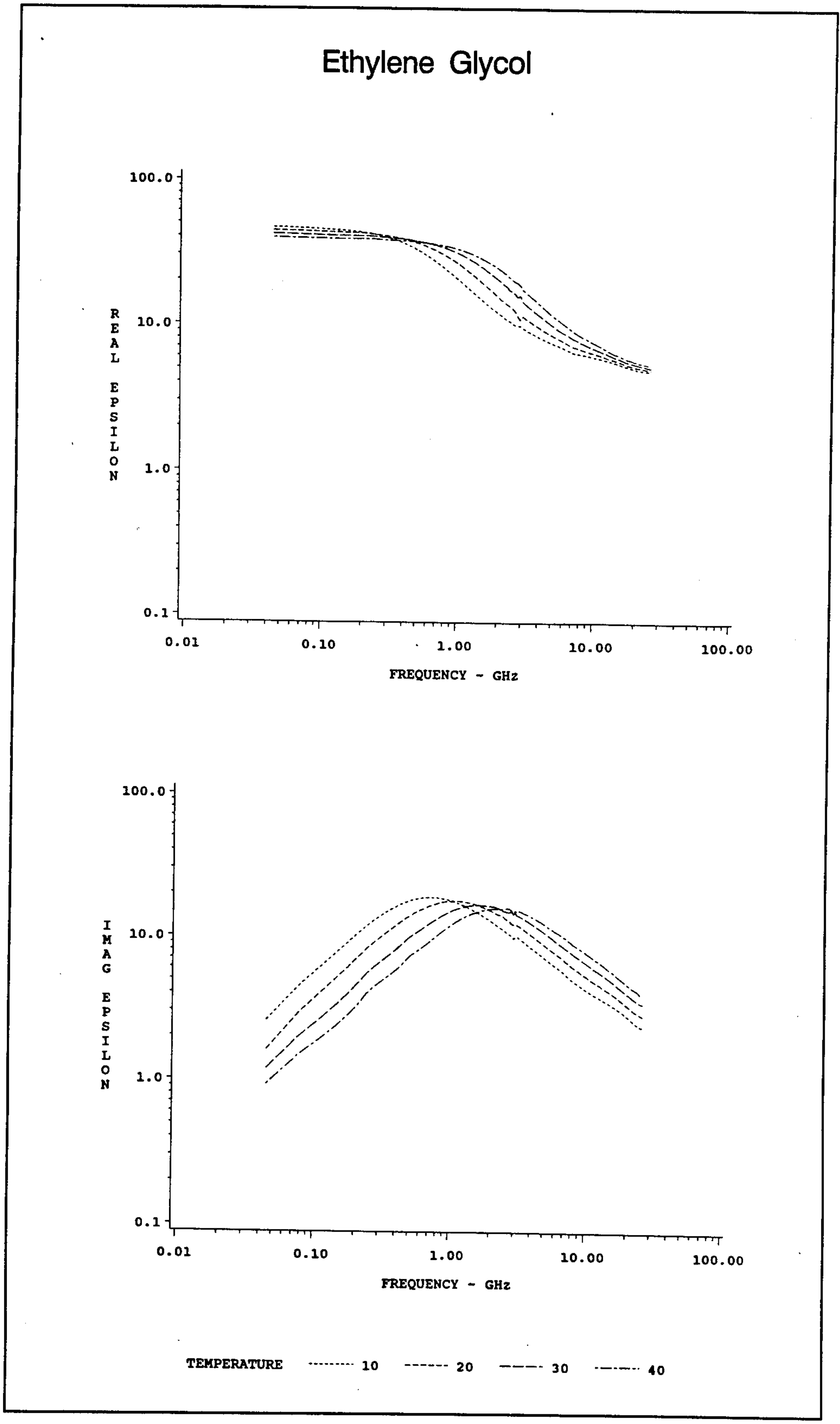


Figure 8. Experimental results for ethylene glycol (Sheet 1 of 3)

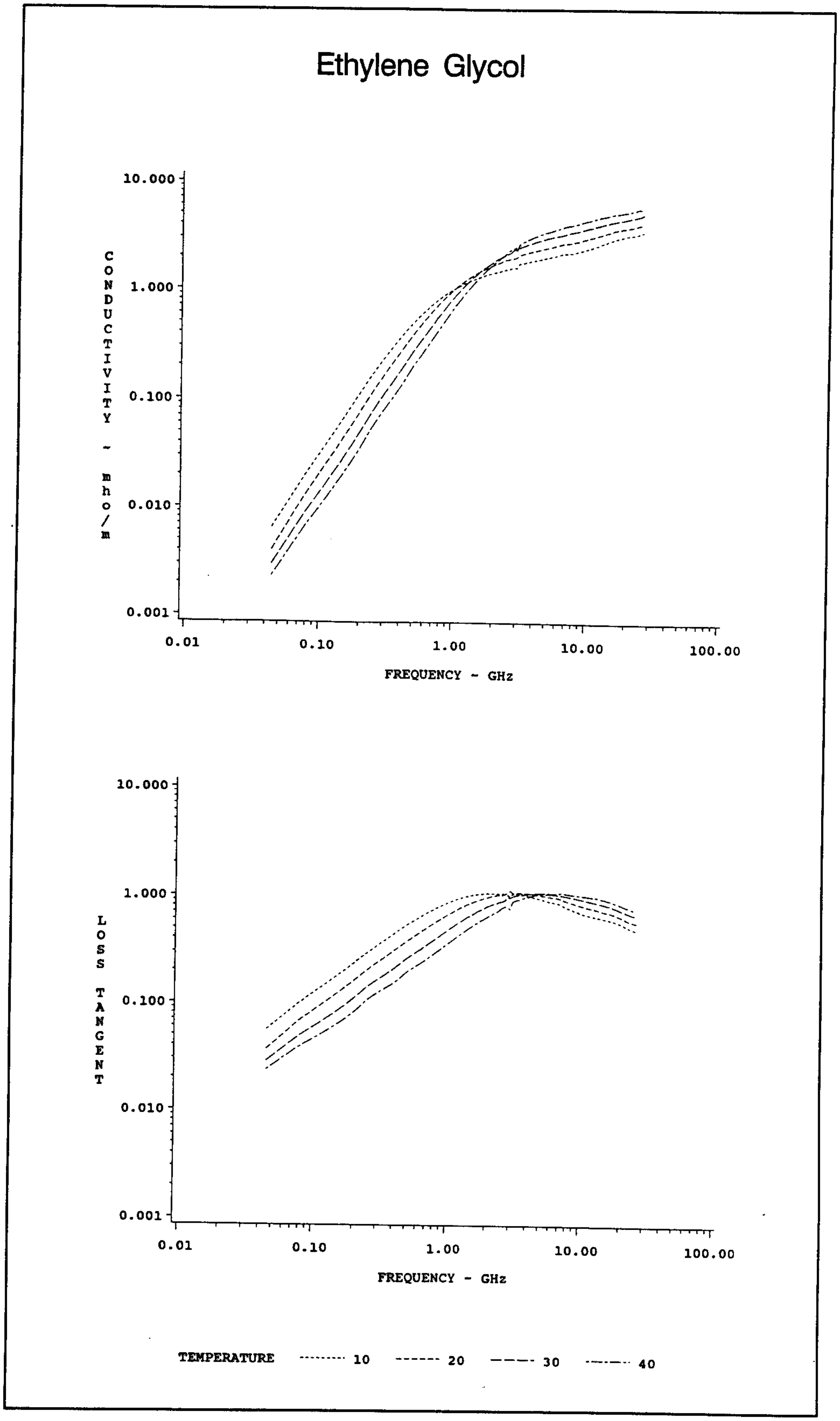


Figure 8. (Sheet 2 of 3)

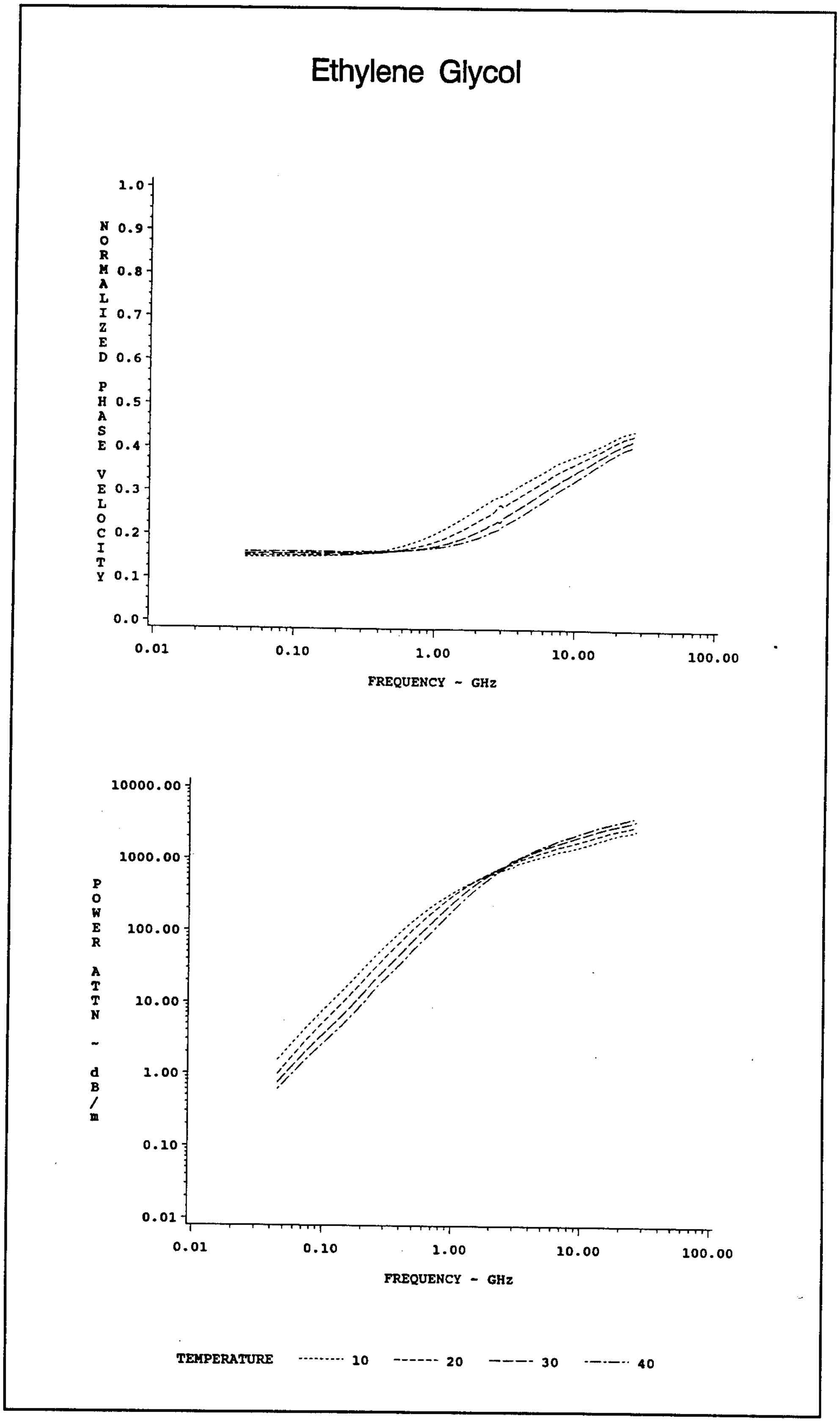


Figure 8. (Sheet 3 of 3)

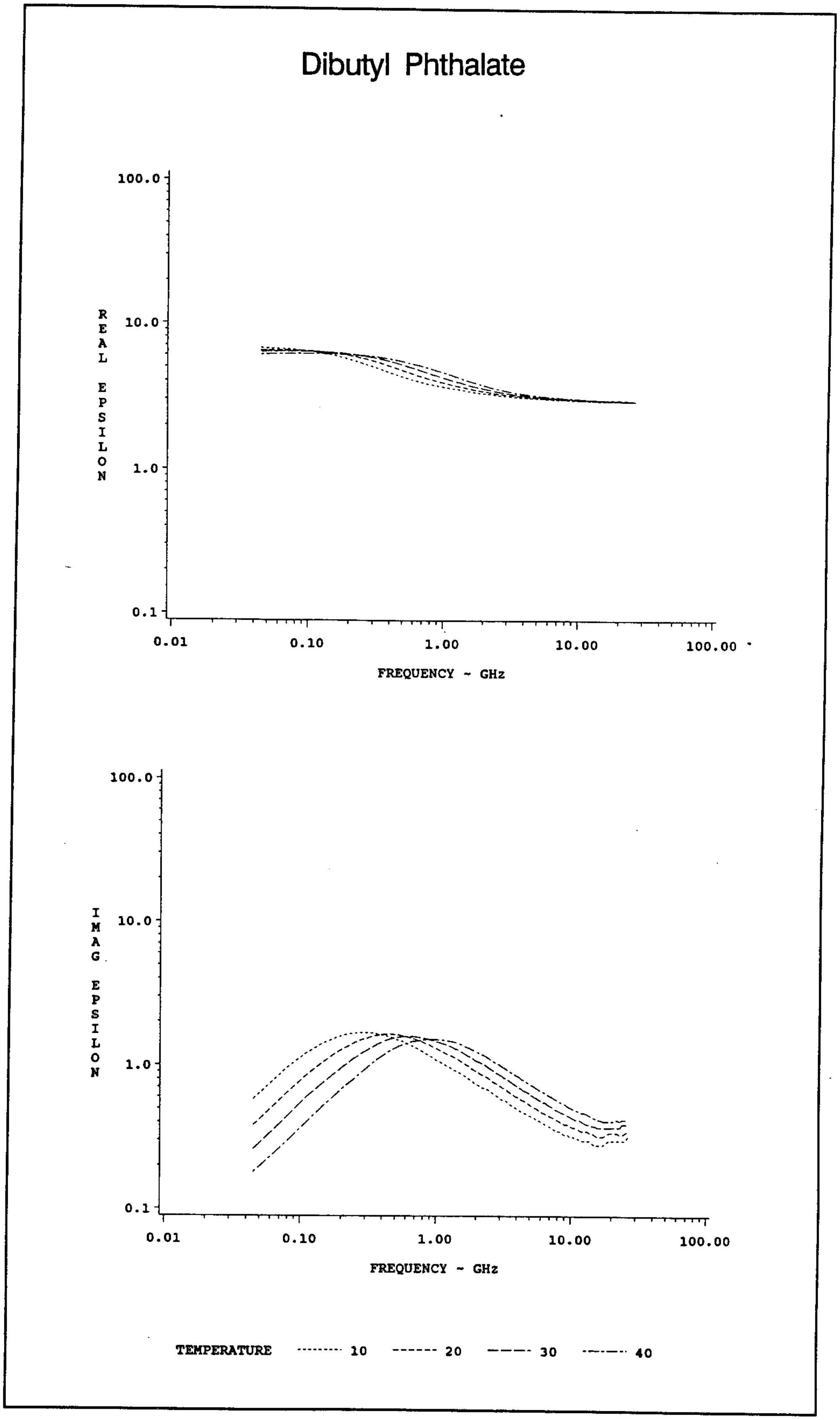


Figure 9. Experimental results for dibutyl phthalate (Sheet 1 of 3)

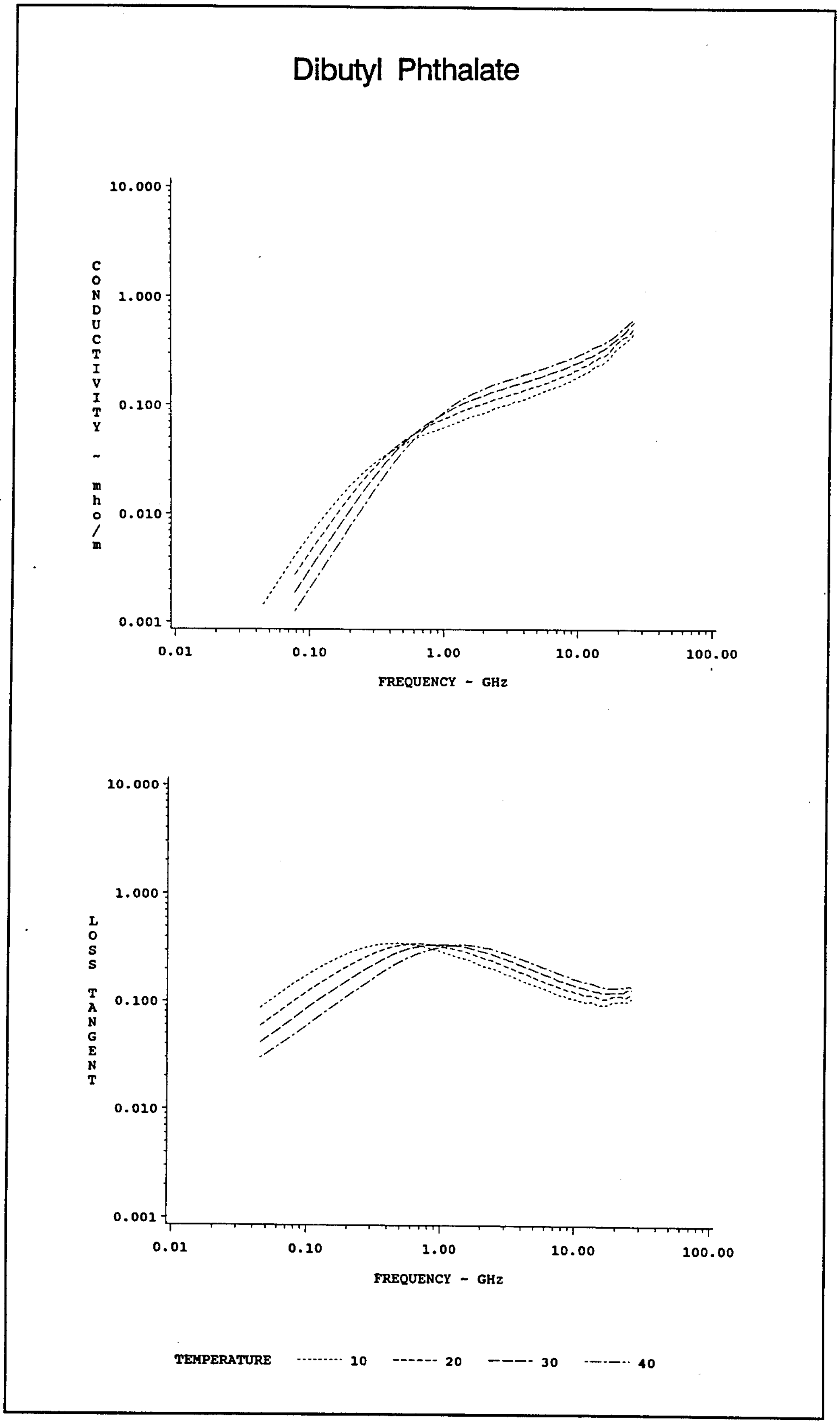


Figure 9. (Sheet 2 of 3)

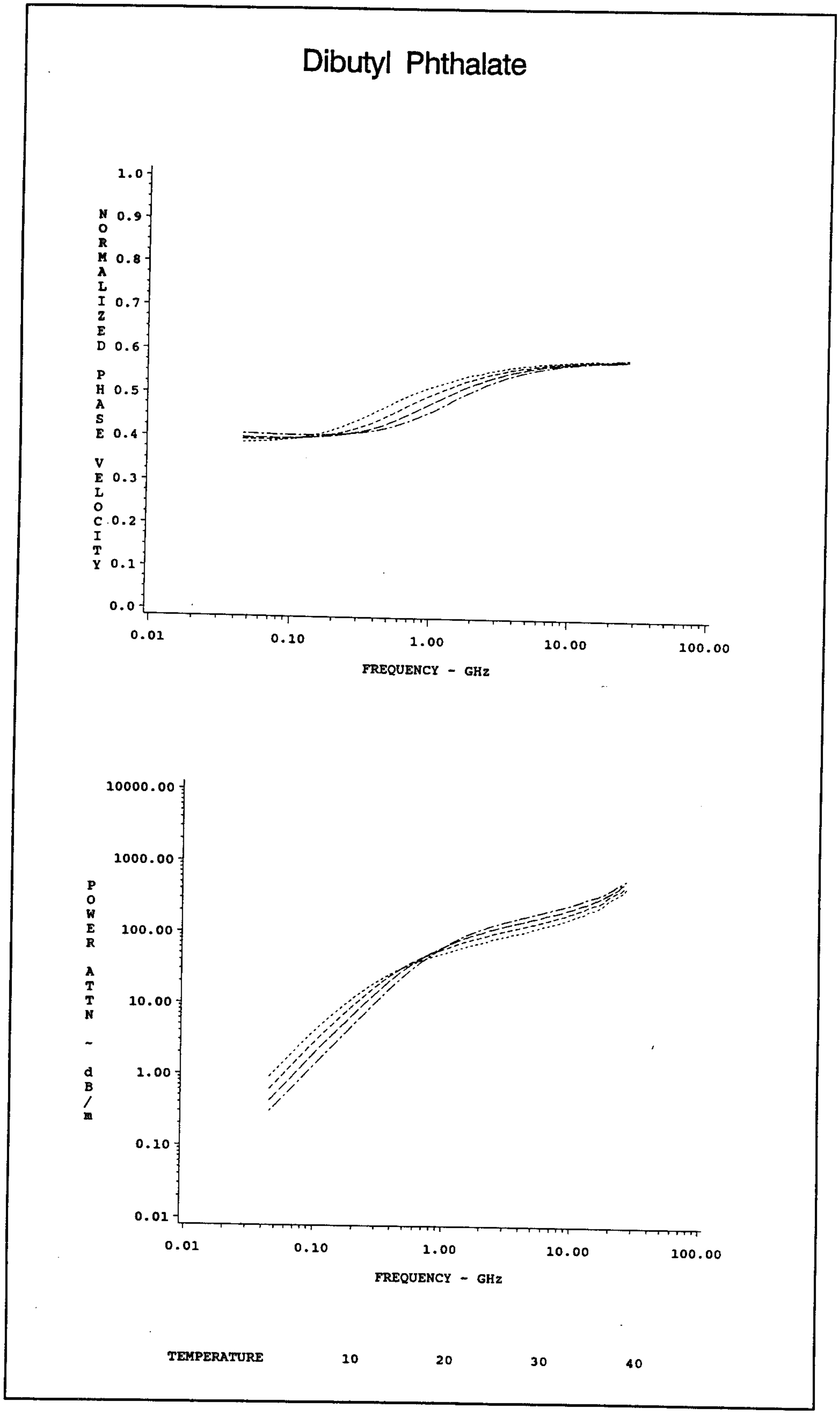


Figure 9. (Sheet 3 of 3)

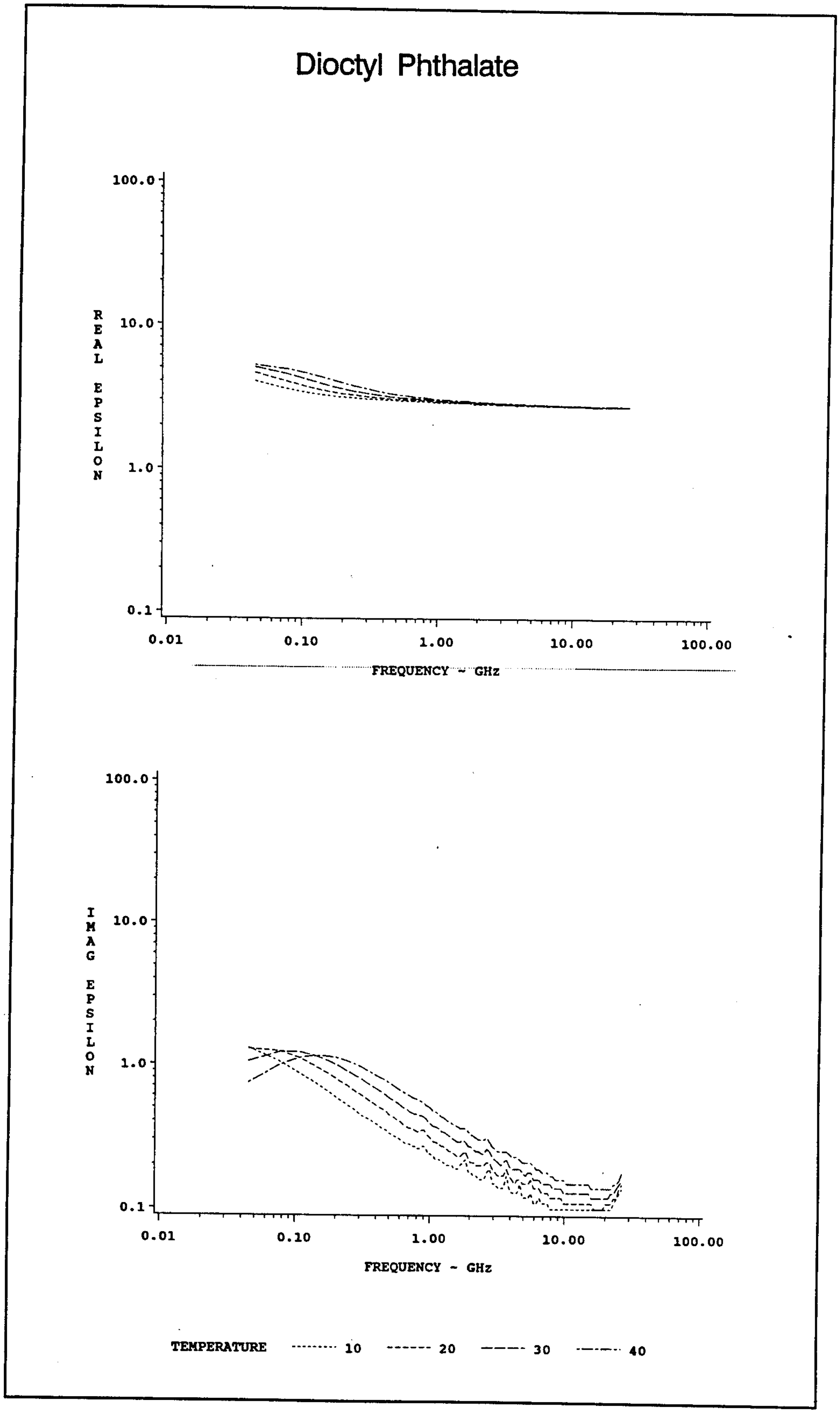


Figure 10. Experimental results for dioctyl phthalate (Sheet 1 of 3)

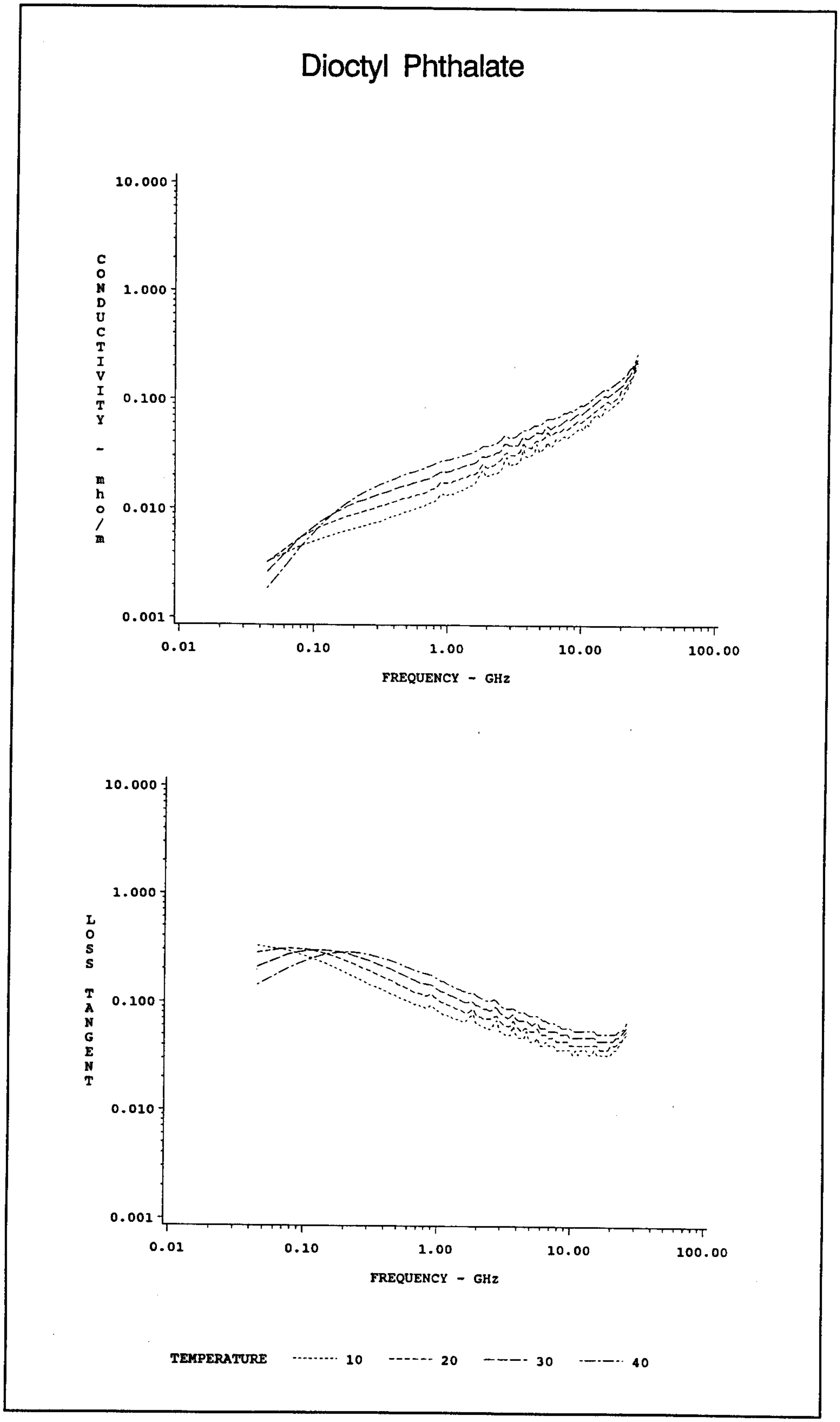


Figure 10. (Sheet 2 of 3)

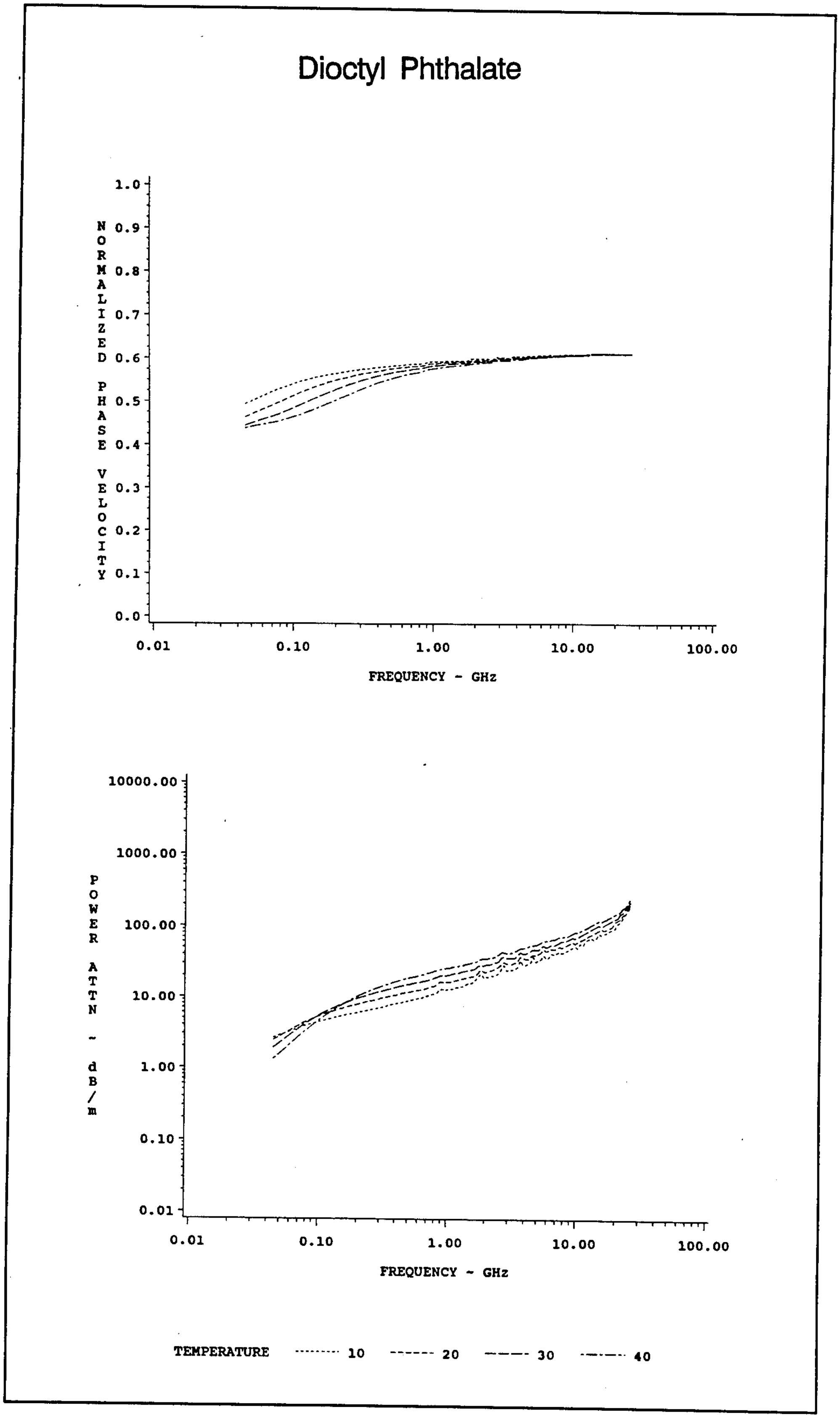


Figure 10. (Sheet 3 of 3)

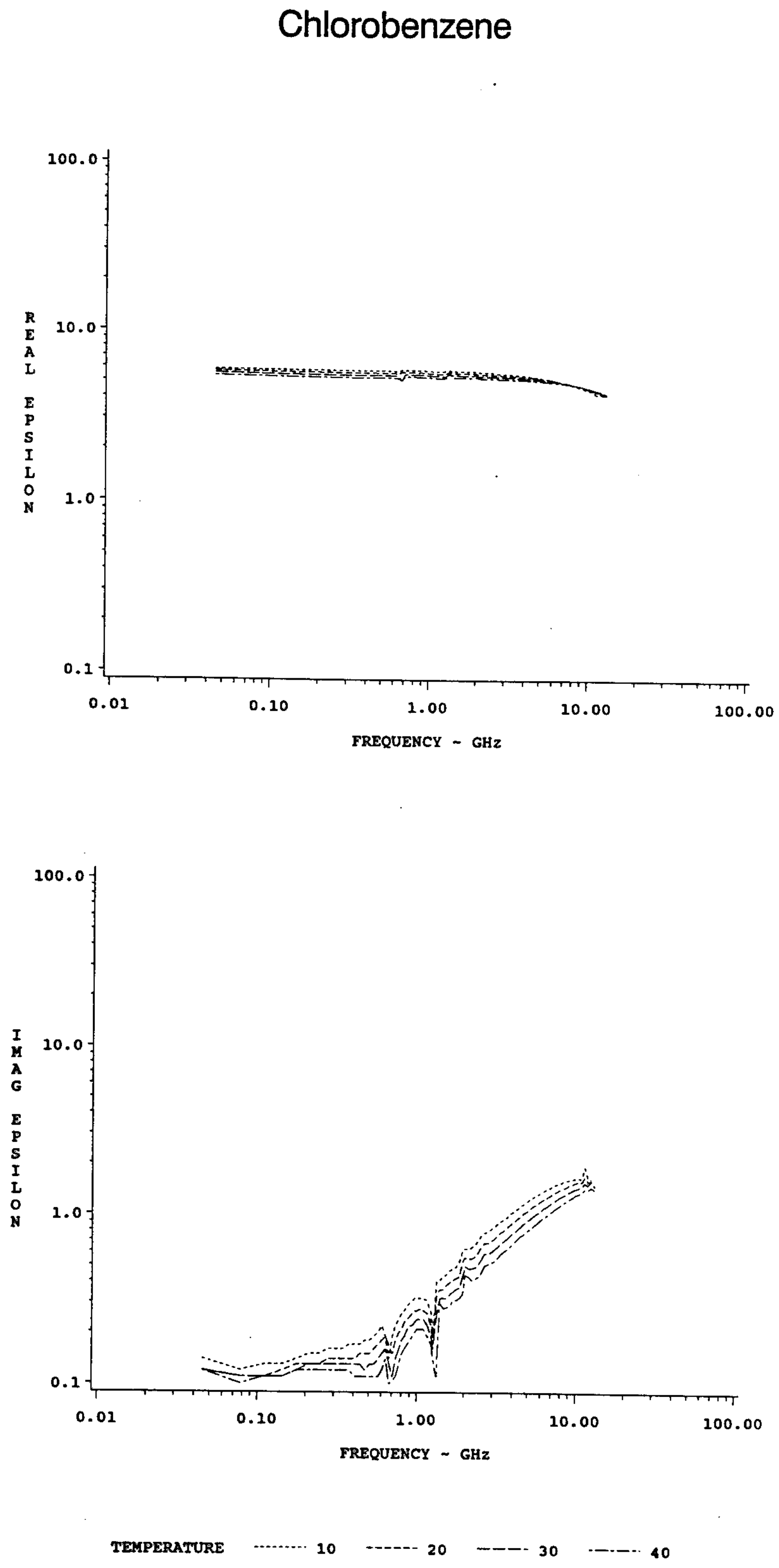


Figure 11. Experimental results for chlorobenzene (Sheet 1 of 3)

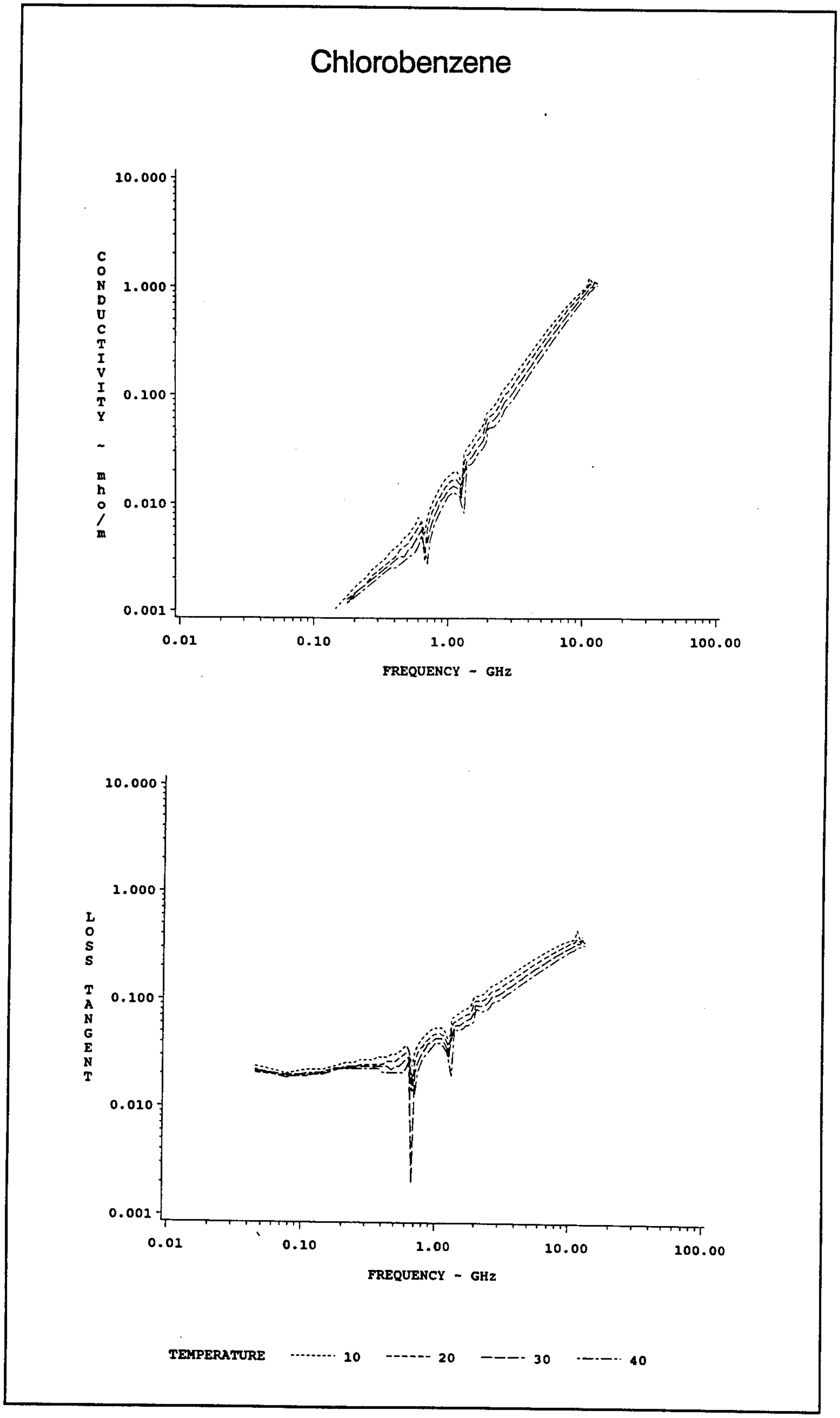


Figure 11. (Sheet 2 of 3)

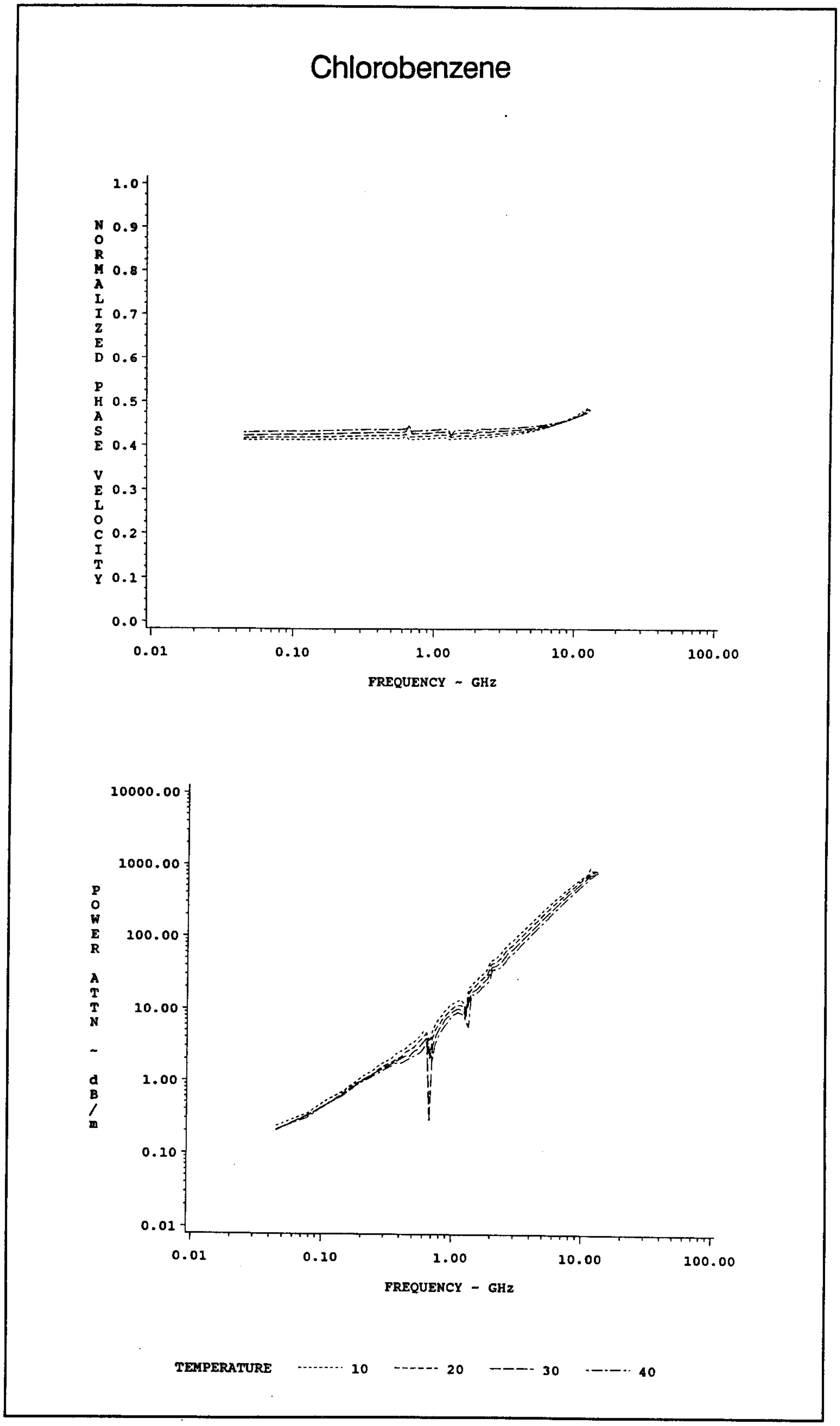


Figure 11. (Sheet 3 of 3)

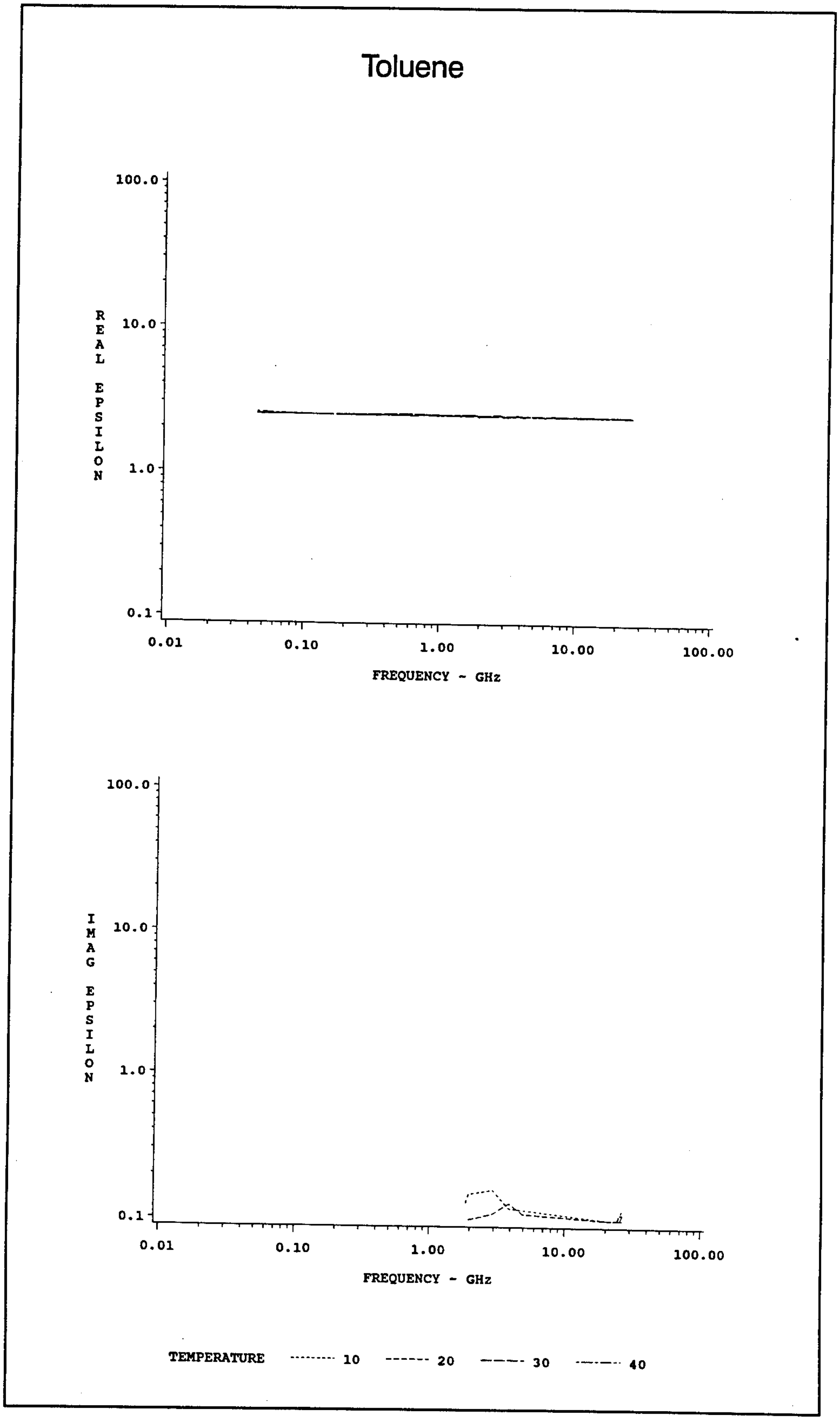


Figure 12. Experimental results for toluene (Sheet 1 of 3)

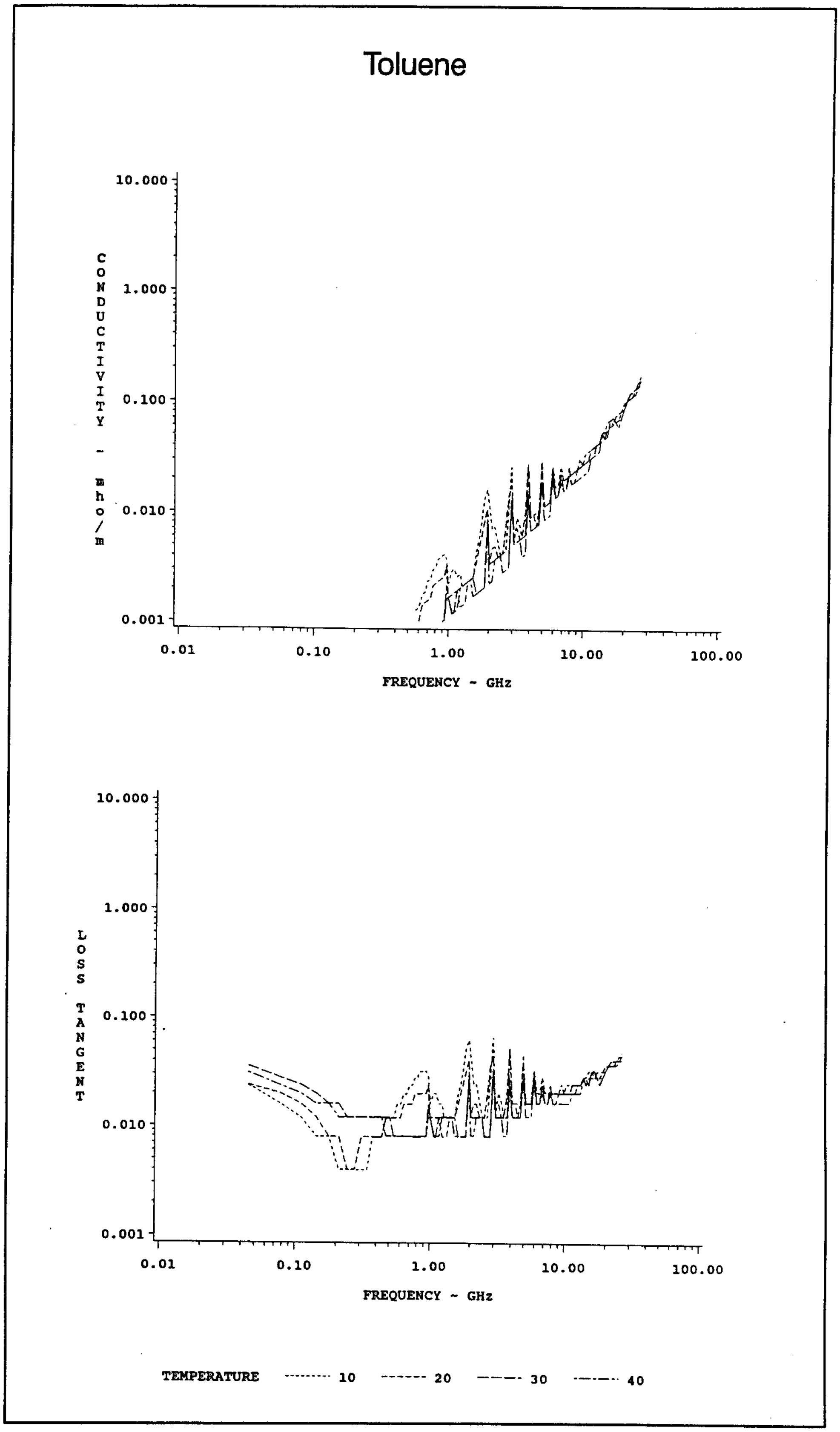


Figure 12. (Sheet 2 of 3)

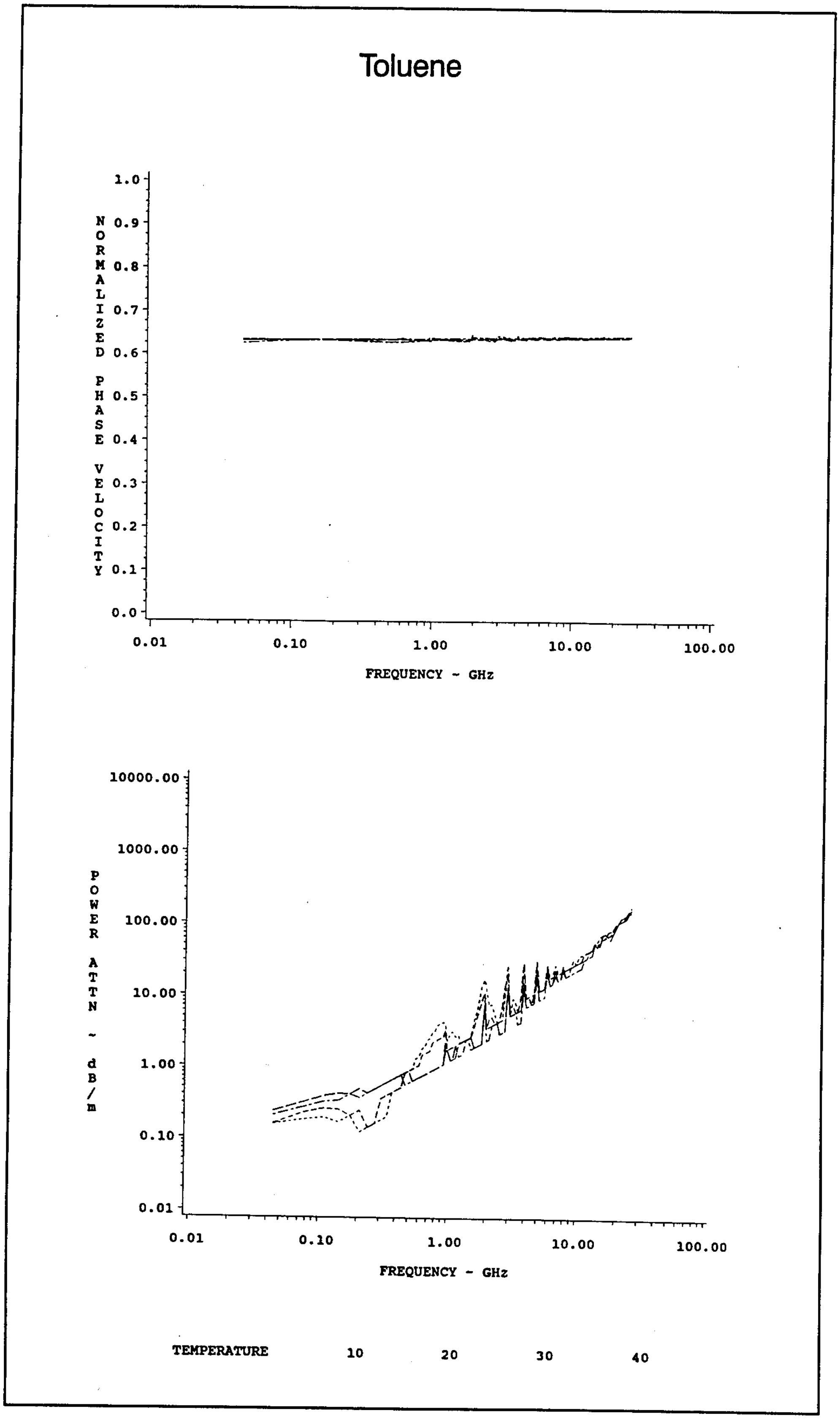


Figure 12. (Sheet 3 of 3)

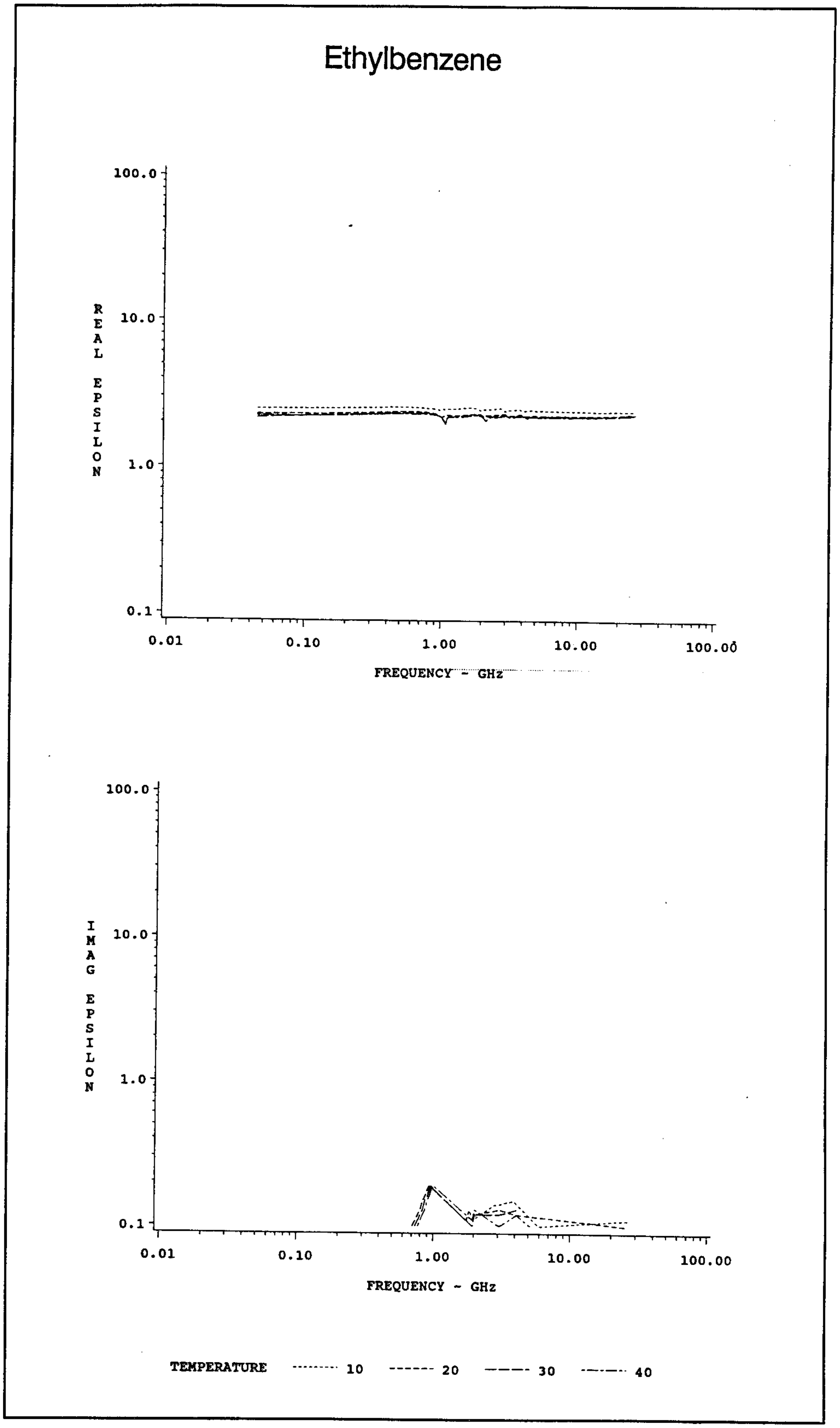


Figure 13. Experimental results for ethylbenzene (Sheet 1 of 3)

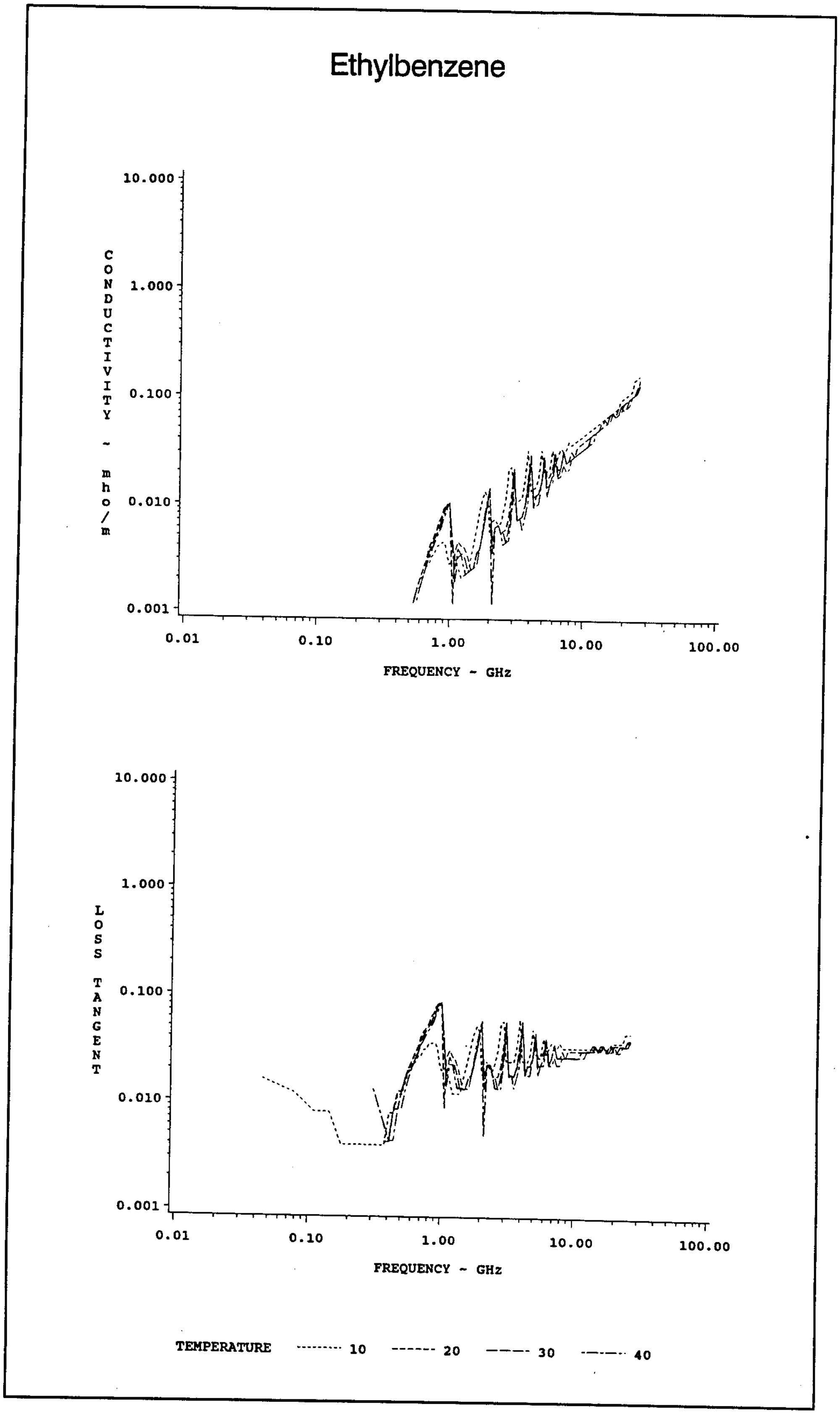


Figure 13. (Sheet 2 of 3)

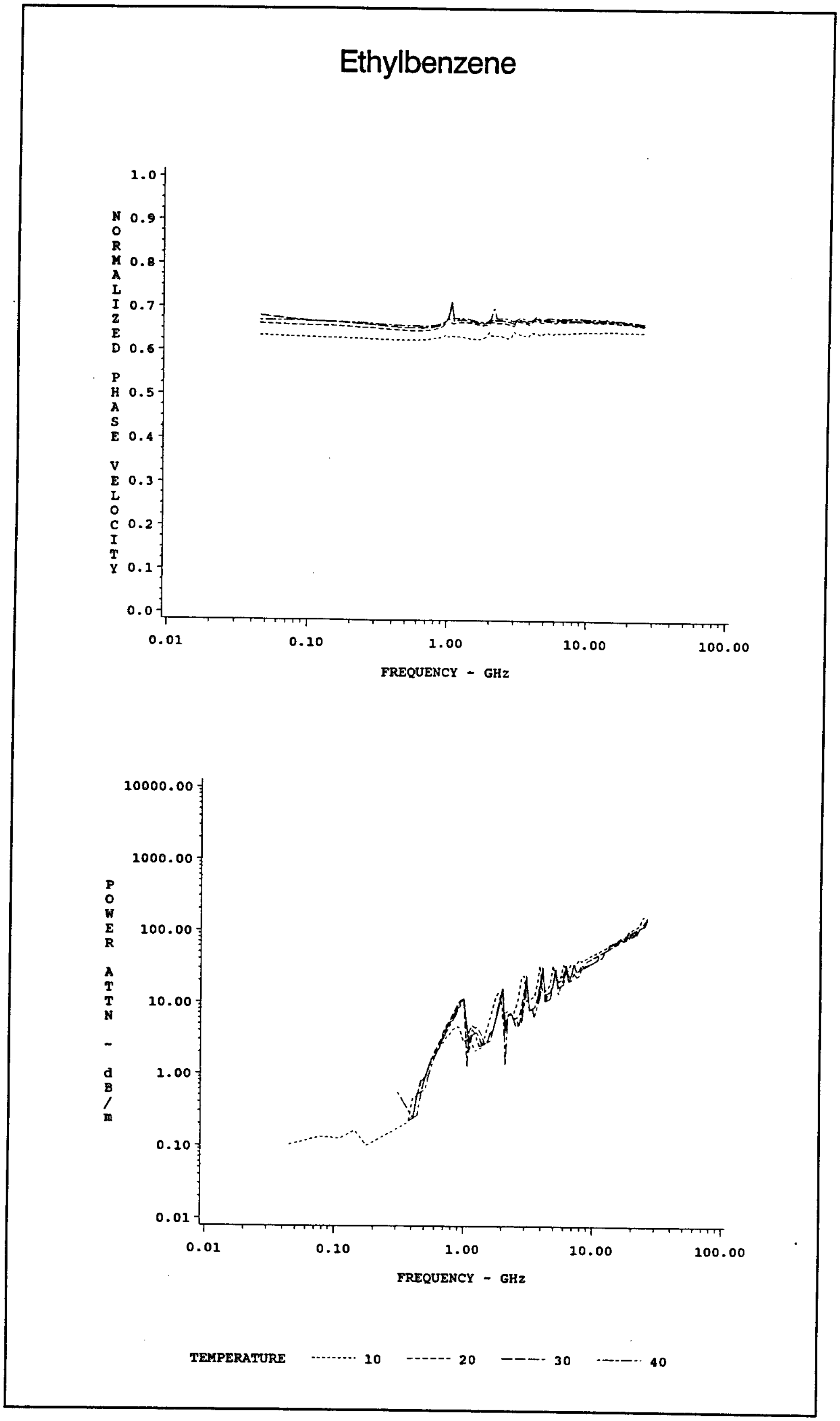


Figure 13. (Sheet 3 of 3)

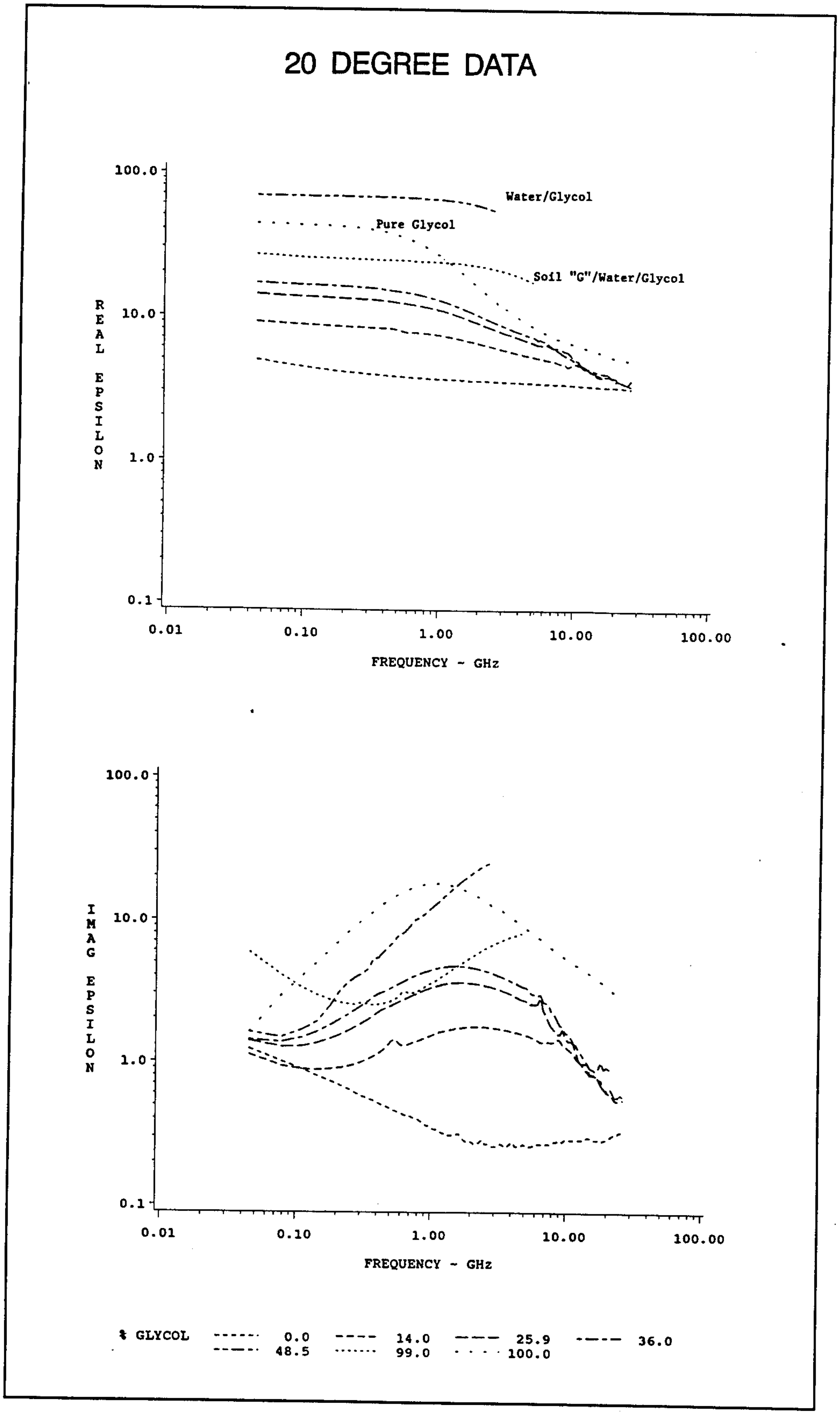


Figure 14. Experimental results for mixtures at 20 °C (Sheet 1 of 3)

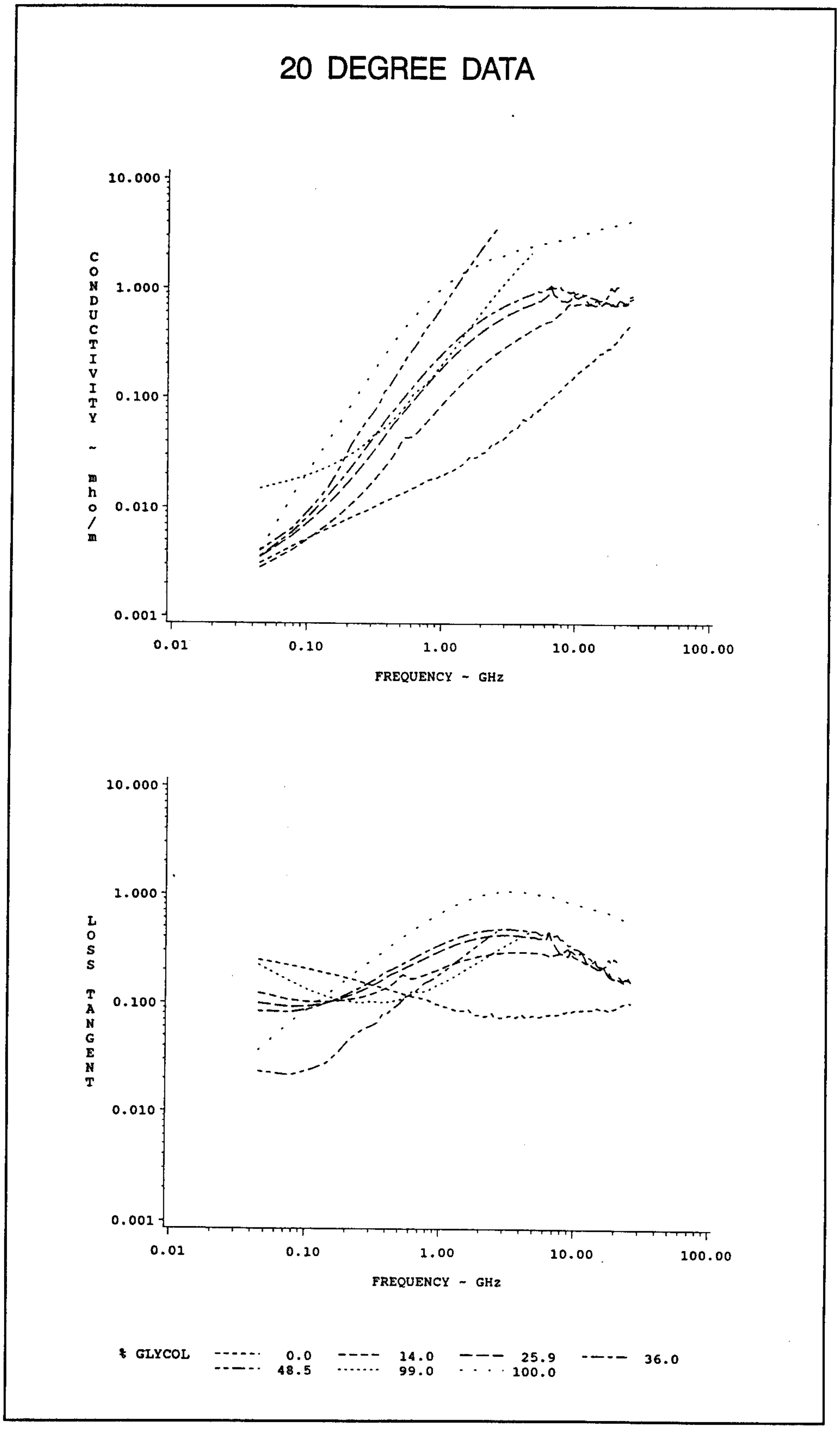


Figure 14. (Sheet 2 of 3)

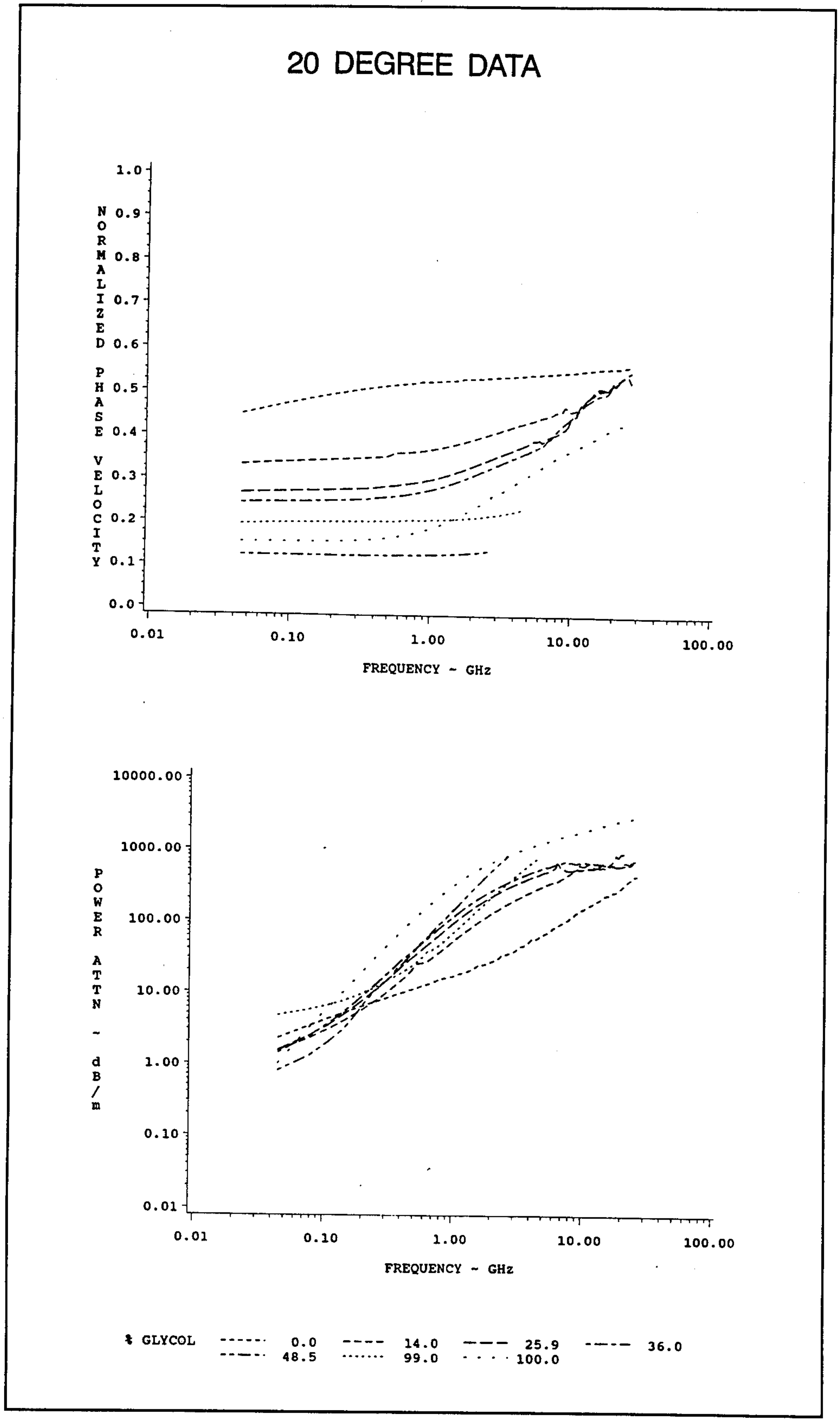


Figure 14. (Sheet 3 of 3)

4 Evaluation of Data

Pure Contaminants

The first question to be answered is whether or not the relative dielectric response of pure contaminants can be predicted from their physical properties. For example, the real part of the complex dielectric constant is an indication of the ability of material molecules to align themselves with the oscillating electric field. The greater the permittivity, the more complete is that alignment and the greater is the effective charge transfer (the classical parallel plate interpretation of added capacitance due to molecular polarization). It would then be sensible that whatever physical properties enhance the response of the material molecules to an oscillating electric field should result in higher permittivity values.

Simple models are available in the literature for predicting the permittivity of a material as a function of physical properties. For example, one source related the behavior of an oscillating electric dipole to the response of a spring-mass-damper mechanical system in which the inertia forces were taken to be insignificant and showed that the zero-frequency (static) permittivity of a substance could be written (Reitz, Milford, and Christy 1980):

$$\epsilon' \ \alpha \ \left[\frac{(Number\ of\ dipoles/volume)\ (Dipole\ moment)^2}{Temperature} \right]$$

Note that the data in Figures 8-13 support the temperature relationship if one assumes that the low-frequency results are not much different from static values.

To better visualize the relative response of the pure contaminants, Figure 15 contains plots of measured and processed data for the six contaminants measured in this study. Using the specific gravity of each contaminant divided by the relative molecular mass as an approximation to the number of dipoles per unit volume and multiplying this number by the square of the permanent dipole moments listed in Table 1, it can be shown that the simple model described above does an effective job of predicting the relative low-frequency permittivities of this group of liquid contaminants.

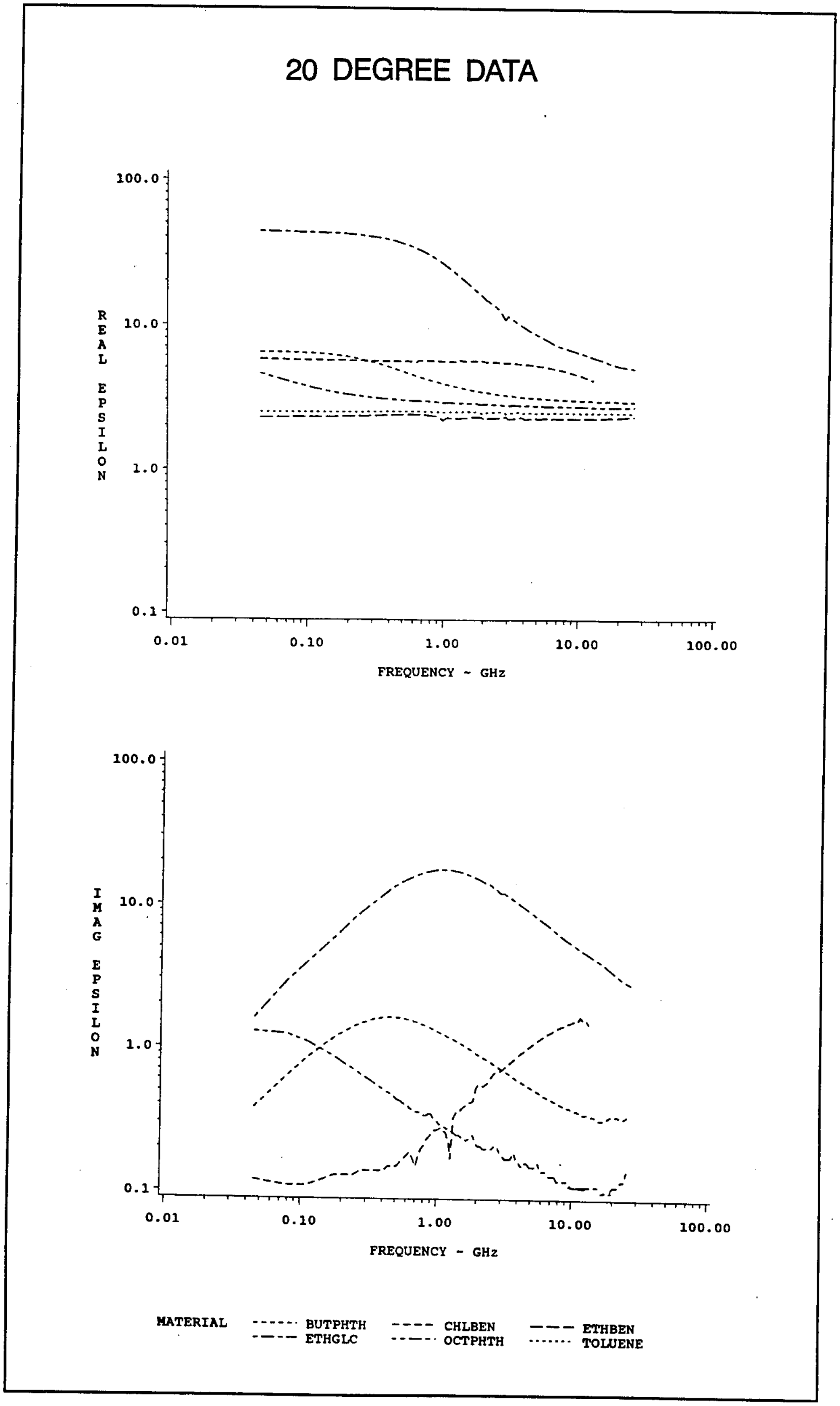


Figure 15. Experimental results for pure contaminants at 20 °C (Sheet 1 of 3)

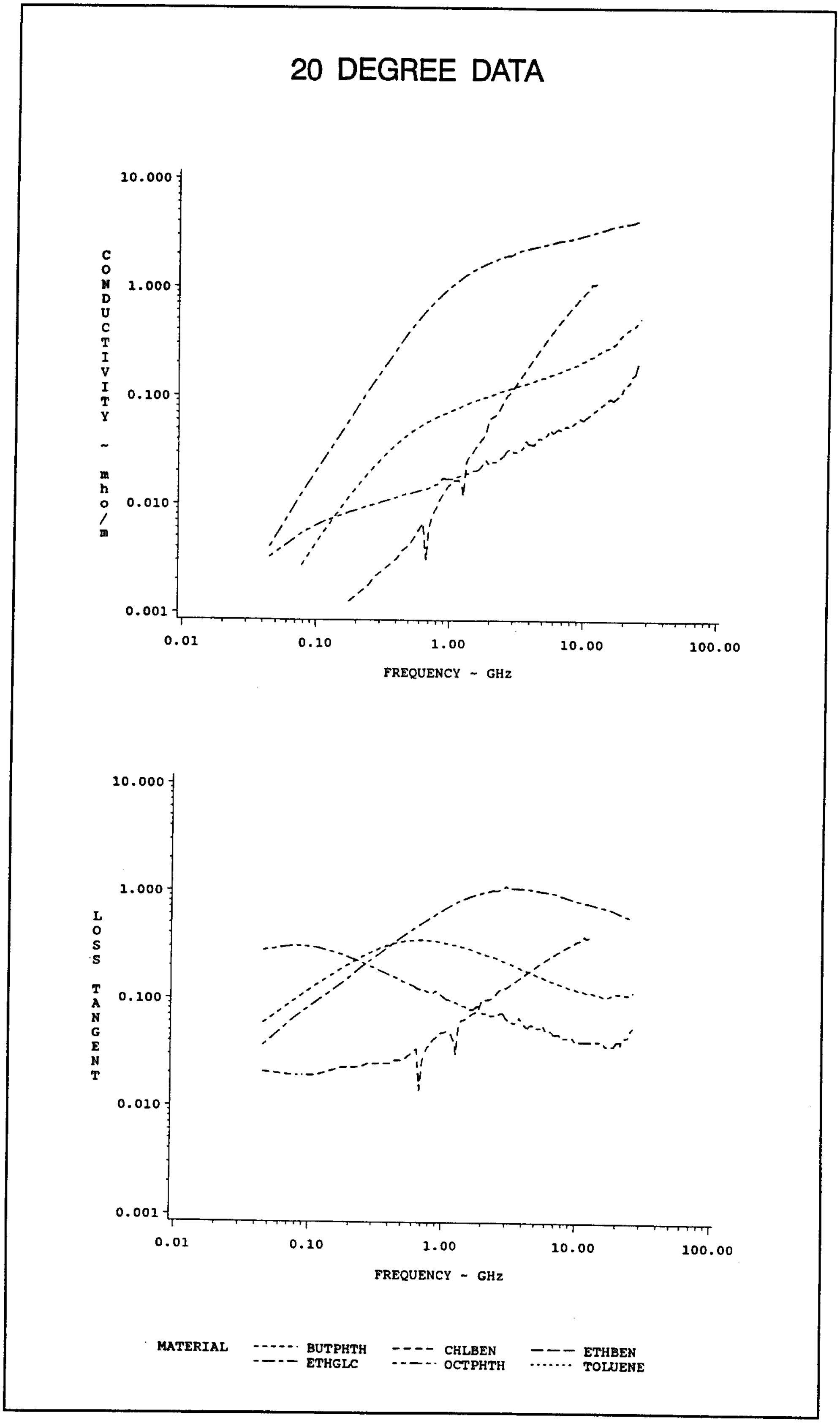


Figure 15. (Sheet 2 of 3)

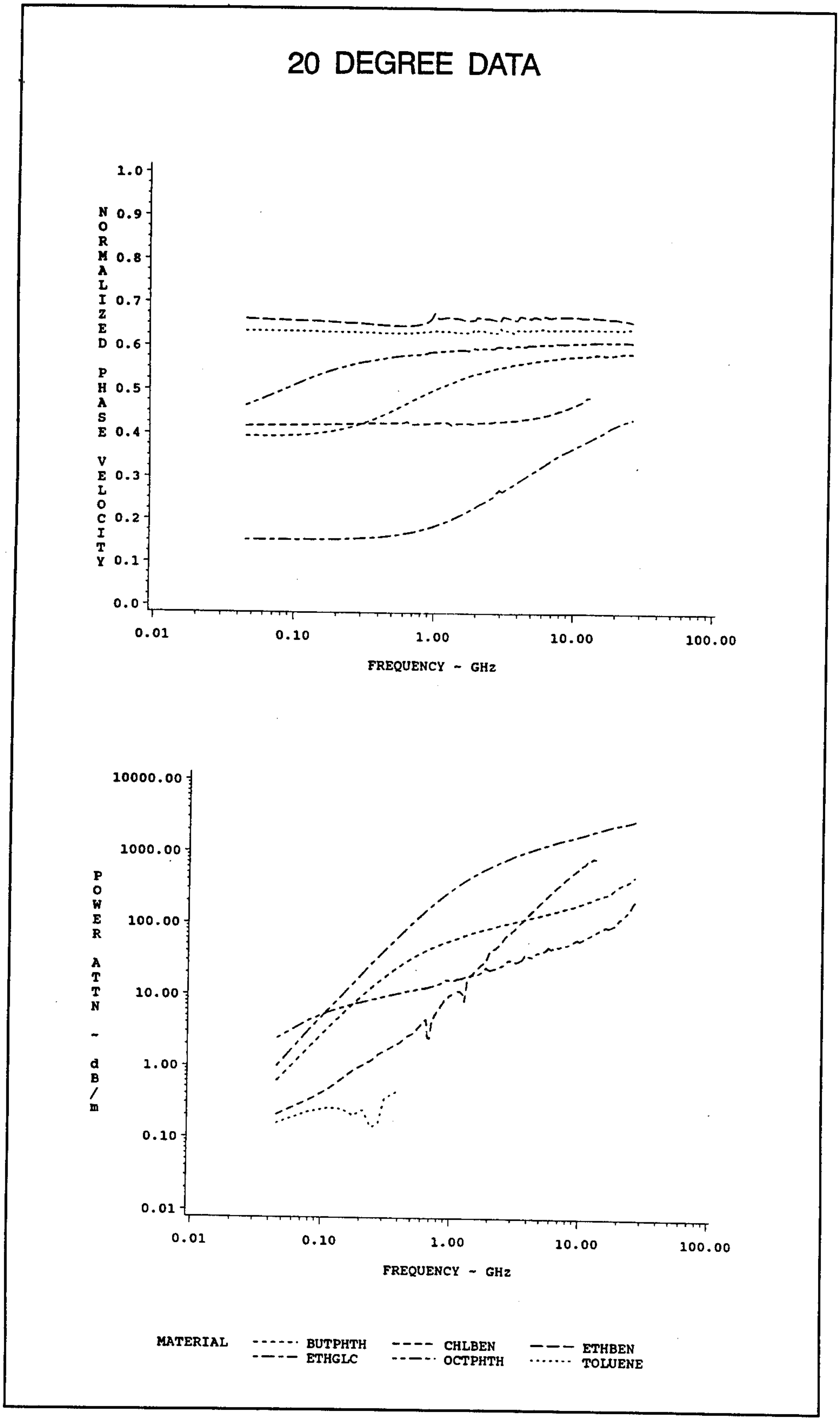


Figure 15. (Sheet 3 of 3)

The plot of imaginary dielectric constant values clearly shows the range of values of the resonant frequency of the material. Again, the question is, are these resonant frequencies reasonable and predictable from physical properties. Debye (Debye 1929) used a simple massless model of polar molecules (molecules possessing a permanent dipole moment) to estimate the order of magnitude of this resonant frequency. His model was one of a sphere of radius, a, rotating in a liquid of viscosity, η, and at a temperature, T. For these conditions, it was found that the resonant frequency could be written:

$$\text{frequency} \; \alpha \; \left[\frac{T}{\eta a^3}\right]$$

Note, as before, that the measurement results shown in Figures 8-13 agree with the prediction that resonant frequency increases with temperature. If one substitutes the strength of the dipole moment for the radius of the sphere, and if one can safely assume that mass (or the mass moment of inertia) should have an inverse relationship with resonant frequency, then the final model for predicting resonant frequencies in these contaminants can be written:

$$\text{frequency} \; \alpha \; \left[\frac{T}{(\eta)(\text{mass})(\text{dipole moment})^3}\right]$$

Once again, using the physical properties listed in Table 1, one finds that the relative values of resonant frequencies are in line with those of the data collected in this study.

Clearly, then, if one knows precisely the complex dielectric response and physical properties of one substance (say, for example, pure water), then one should be able to predict the relative response of other substances from their physical properties.

Mixtures

The second question to be answered is whether or not the dielectric response of mixtures of substances, as measured in this study, can be described by simplistic models. For example, the capacitance of an idealized, lossless parallel plate capacitor is related to the permittivity of the dielectric material between its plates, the area of the plates, and the spacing of the plates. If one wished to model the dielectric response of a mixture of materials, then it might be possible to develop an electrical circuit with capacitors representing the contributions of each component. The implicit assumption in this mixture modeling is that the properties (in this case, permittivity) of the component substances are not changed in the mixture. In other words, the mixture components do not undergo any chemical changes.

Consider the extremes of such mixing models. On the one hand, one might have a simple capacitor with different dielectric materials inserted between the plates in the fashion shown in Figure 16a. The name given to such an arrangement would be parallel mixing, as the current in this circuit follows three parallel paths, each of which experiences the same voltage drop. Charge builds up on each section of the plate in an amount equal to the product of the capacitance of the material and the voltage difference across the plate. The total charge on either plate can then be written in terms of the component permittivities:

$$Q = Q_g + Q_l + Q_s = C_g V + C_l V + C_s V$$

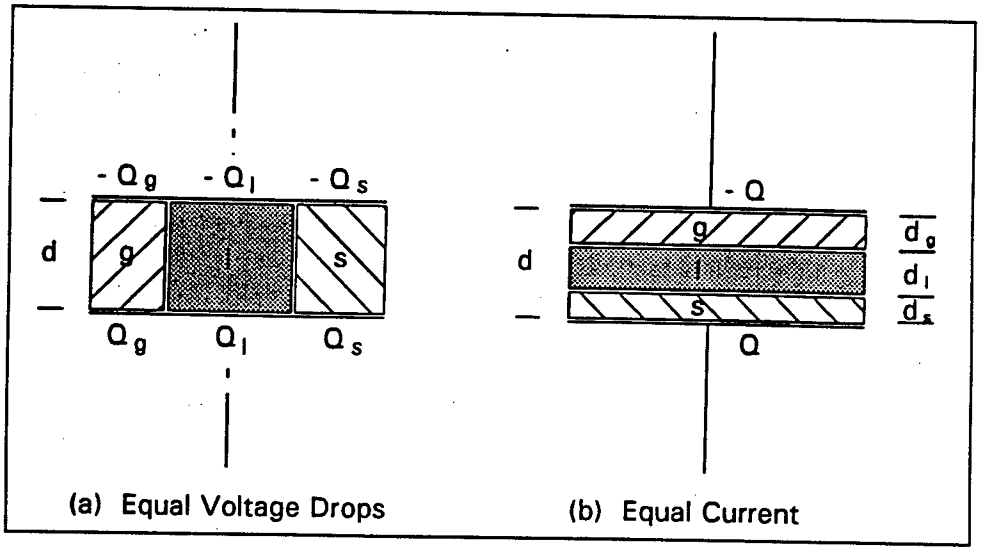
$$= V\left[\frac{\epsilon_g A_g}{d} + \frac{\epsilon_l A_l}{d} + \frac{\epsilon_s A_s}{d}\right]$$

or

$$\frac{Q}{V} = C_{mixture} = \frac{\epsilon_{mix} A}{d} = \frac{\epsilon_g A_g}{d} + \frac{\epsilon_l A_l}{d} + \frac{\epsilon_s A_s}{d}$$

Finally,

$$\epsilon_{mixture} = \left[\frac{A_g}{A}\right]\epsilon_g + \left[\frac{A_l}{A}\right]\epsilon_l + \left[\frac{A_s}{A}\right]\epsilon_s$$



(a) Equal Voltage Drops (b) Equal Current

Figure 16. Mixing model electrical analogues

In words, the effective permittivity of a mixture of these three substances is the weighted sum of the individual permittivities. The weighting factors are the respective area fractions for each substance, which, for the parallel plate geometry shown, is the same as volume fraction.

The other extreme for an electrical analogue for mixing is that of the geometry shown in Figure 16b, where the different materials are sandwiched between the plates of the capacitor. The name given to this arrangement would be series mixing, as there is only one channel for current flow, and the same current passes through each sandwich layer. In this situation, the total voltage across the plates is the sum of the voltage differences across each layer:

$$V = \frac{Q}{C_{mixture}} = V_g + V_l + V_s = \frac{Q}{C_g} + \frac{Q}{C_l} + \frac{Q}{C_s}$$

Making the same substitutions for capacitance in terms of permittivity, plate area, and layer thicknesses as above, one has

$$\frac{d}{\epsilon_{mix} A} = \frac{d_g}{\epsilon_g A} + \frac{d_l}{\epsilon_l A} + \frac{d_s}{\epsilon_s A}$$

or

$$\frac{1}{\epsilon_{mix}} = \left[\frac{d_g}{d}\right]\frac{1}{\epsilon_g} + \left[\frac{d_l}{d}\right]\frac{1}{\epsilon_l} + \left[\frac{d_s}{d}\right]\frac{1}{\epsilon_s}$$

As before, for the geometry shown in Figure 16b, the thickness ratios are equivalent to volume fractions.

Given these extreme mixture scenarios, it is not surprising that one can write, as a generalization of such mixture models, the following expression (Ansoult, DeBacker, and DeClercq 1984):

$$\epsilon_m{}^k = W_g \epsilon_g{}^k + W_l \epsilon_l{}^k + W_s \epsilon_s{}^k \qquad (9)$$

where, for this study, the subscripts stand for "mixture," "gas," "liquid," and "solid." The *W*'s are weighting factors associated with each component of the mixture and are, as argued above, the respective volume fractions.

The exponent of the permittivity terms can vary between +1 and -1. Clearly, the exponent of +1 is the parallel mixing model, and the exponent of -1 is the series mixing model. In the absence of chemical reactions, permittivities of real mixtures should lie somewhere between these bounds.

Now is the time to compare the data collected in this study against the generalized model. Hopefully, this will answer the questions posed in the introductory chapter on what mixtures follow a particular mixing law. However, before exercising the generalized model, one must select certain frequencies, calculate the volume fractions for the constituents, and tabulate the measured permittivities. Volume fractions for all of the mixture measurements are shown in Table 4.

Table 4
Volume Fractions Used for Mixture Modeling

Material(s)	W_{solid}	W_{liquid}		W_{gas}
Soil (SG=2.66)	0.524	0.000 (assumed)		0.476
Soil + 14 percent Glycol	0.524	0.140		0.336
Soil + 25.9 percent Glycol	0.524	0.259		0.217
Soil + 36 percent Glycol	0.524	0.360		0.116
100 percent Glycol	0.000	1.000		0.000
Water/Glycol	0.000	0.515 (W)	0.485 (G)	0.000
Soil/Water/Glycol	0.553	0.234 (W)	0.200 (G)	0.013
Water	0.000	1.000		0.000

Table 5 is a tabulation of the permittivities for all of the mixtures and pure constituents for three frequencies, 45, 210, and 508 MHz. These frequencies were selected to fall within the normal operating range of ground-penetrating radars and to avoid the range of frequencies affected by the dielectric relaxation phenomenon in both water and ethylene glycol.

Table 5
Measured Values of Permittivity at Three Frequencies

Material(s)	45 MHz	210 MHz	508 MHz
Soil/Air	4.94	4.08	3.80
Calculated Pure Solid	12.06	7.96	6.82
Soil + 14 percent Glycol	9.08	8.44	8.02
Soil + 25.9 percent Glycol	14.12	13.27	12.38
Soil + 36 percent Glycol	16.94	16.10	14.86
100 percent Glycol	43.81	42.16	36.56
Water/Glycol	68.65	68.52	67.64
Soil/Water/Glycol	26.63	25.21	24.63
Water	82.13	81.68	81.12

Note that the permittivities for dry soil were not labeled as being for soil only. Although the permittivity of air is only unity, it can have a significant impact on the behavior of the mixture (particularly for series mixing) and must be taken into account. In order to force the mixing model to give the correct results for the dry soil measurements, a supplementary calculation had to be performed to compute the pure, solid, soil permittivity for the selected mixing coefficient before exercising the model over the entire range of moisture contents. From the generalized mixing model (Equation 9) this calculation takes the form of:

$$\epsilon_{solid} = \left[\frac{\epsilon^{k}_{dry\ soil\ measurement} - W_{air}}{W_{solid\ soil}} \right]^{\frac{1}{k}}$$

The results of these calculations are found in the second row of Table 5 for the optimum mixing law exponents found by exercising the mixing model as reported in the next section. The numbers for pure solid permittivity are very much in line with published data on solid rock and on powdered rock compressed to densities comparable with the particle density of the soil (Nelson, Lindroth, and Blake 1989; Ulaby et al. 1990).

Soil/glycol mixtures

Figures 17-19 contain the results of soil/glycol mixture permittivity predictions using Equation 9, the volume fraction values in Table 4, and a selected range of exponent values. The three figures use solid soil and pure glycol component permittivity values listed in Table 5 (unit permittivity for air) for 45, 210, and 508 MHz data, respectively. Also plotted on these figures are the mixture permittivity values measured in this study, shown as plus signs.

The first observation that can be made about these results is that the data appear to be fairly well fit by a mixing law with an exponent that falls within the idealized bounds of plus and minus one. Although this is not proof that chemical reactions are not taking place, it does indicate that nothing highly unusual is happening. The real response of the mixture lies somewhere between a parallel mixing law and a series mixing phenomenon.

The second observation is that the exponent of the mixing law is a function of the frequency of the signal passing through the soil. A visual inspection of the comparisons of measured data and model predictions resulted in the values of mixing law exponents listed in Table 6. It would be unwise, at this time, to attempt to associate any physics with this observation. One reason is that as signal frequency increases, the physical mechanisms that result in losses change.

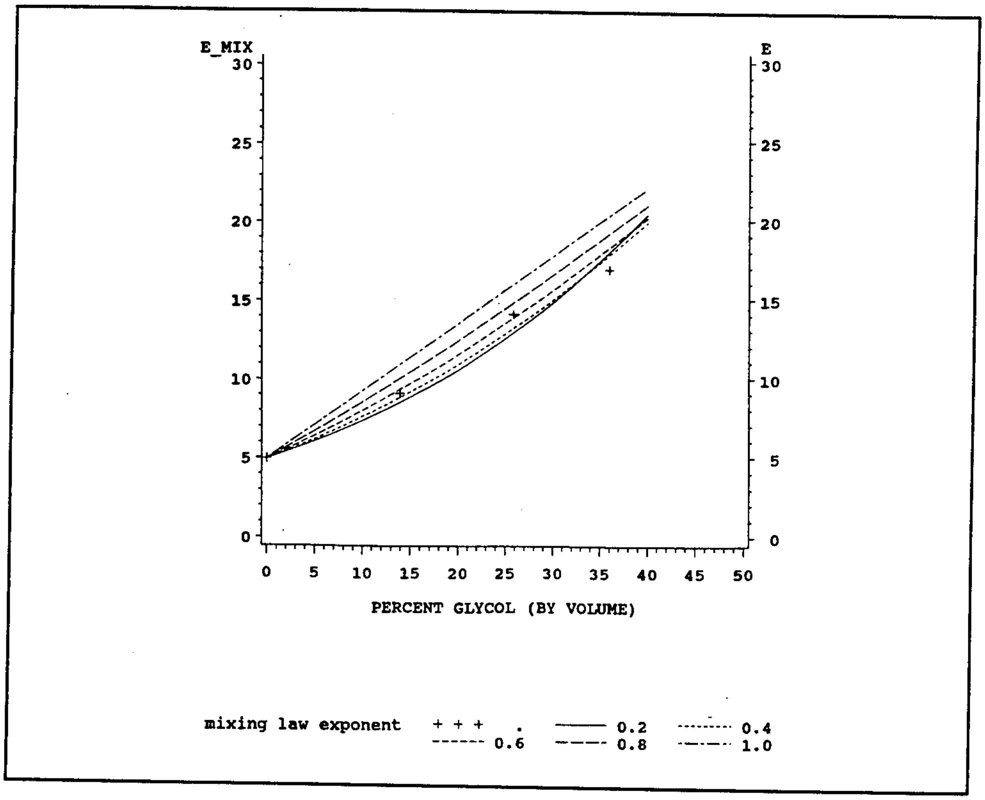


Figure 17. Soil/glycol mixture data and model predictions at 45 MHz

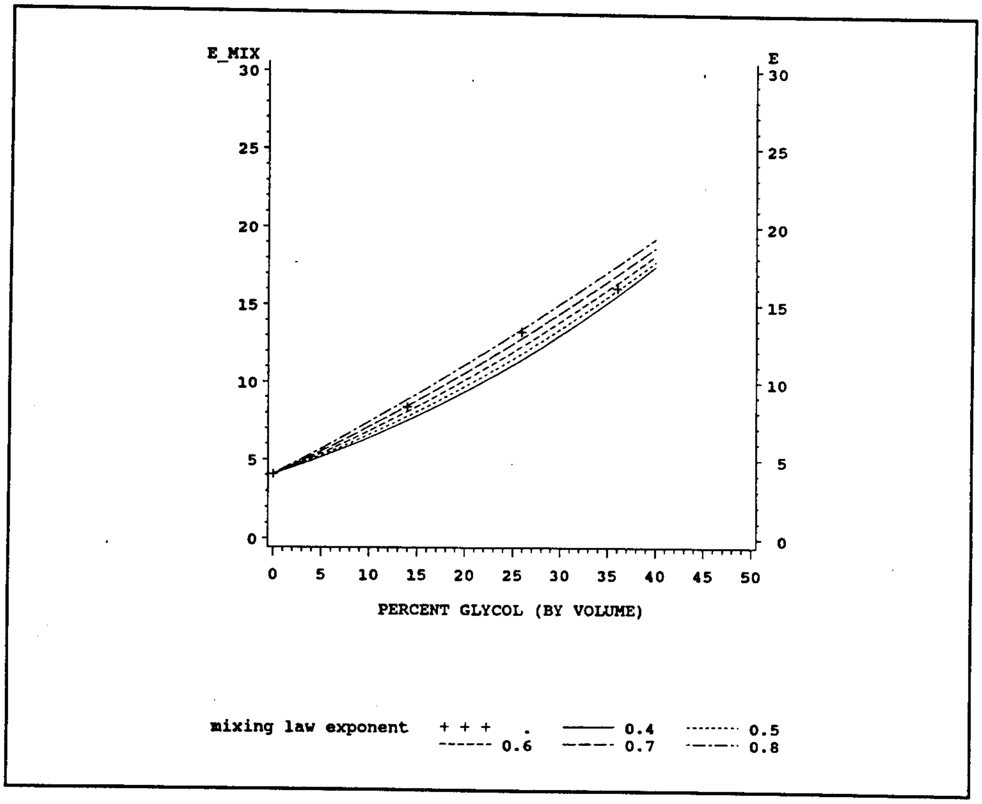


Figure 18. Soil/glycol mixture data and model predictions at 210 MHz

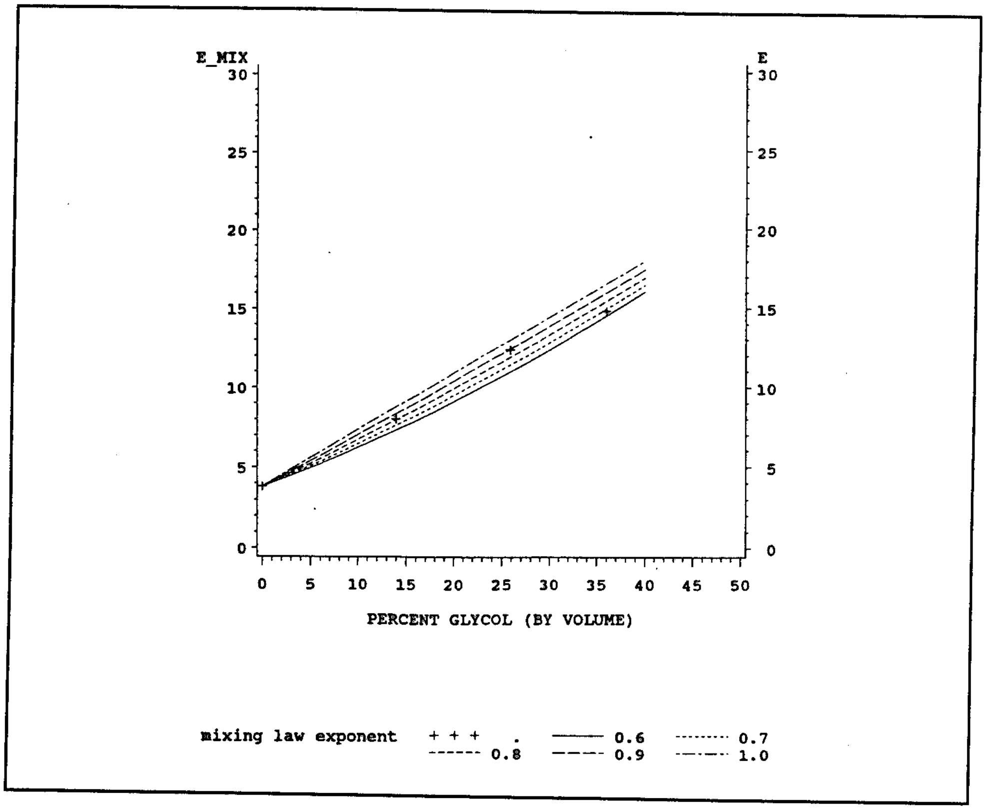


Figure 19. Soil/glycol mixture data and model predictions at 508 MHz

Table 6
Mixing Law Exponents for Soil/Ethylene Glycol Mixtures

Frequency, MHz	Mixing Law Exponent
45	0.40
210	0.65
508	0.80

Soil/water/glycol mixture predictions

Establishing mixing law exponents for specialized conditions is not useful unless they can be applied to other similar problems. During the conduct of this study, one string of data was collected for a mixture of the same soil referenced above, pure ethylene glycol, pure water, and air. If the mixing law exponents determined in the previous section have any validity, and if the addition of one more component to the mixture does not violate any of the mixing model constraints, then the model should provide a reasonable prediction for the dielectric response of this new mixture. The mixing law now is:

$$\epsilon_{mix} = \left[W_{solid}\epsilon_{solid}^{k} + W_{water}\epsilon_{water}^{k} + W_{glycol}\epsilon_{glycol}^{k} + W_{air}\epsilon_{air}^{k}\right]^{\frac{1}{k}}$$

As before, the volume fractions for the soil/air/water/glycol mixture are listed in Table 4, and the pure component permittivities are listed in Table 5. The results of these calculations are shown in Table 7. The agreement with measured data is quite good, with the predicted results being slightly high.

Table 7
Mixing Model Predictions for Soil/Water/Glycol/Air and Water/Glycol Mixtures

Frequency MHz	Mixing Law Exponent	ϵ_{solid}	ϵ_{water}	ϵ_{glycol}	Soil/Water/Glycol/Air Mixture		Water/Glycol Mixture	
					$(\epsilon_{mix})_{predicted}$	$(\epsilon_{mix})_{measured}$	$(\epsilon_{mix})_{predicted}$	$(\epsilon_{mix})_{measured}$
45	0.40	12.06	82.13	43.81	27.81	26.63	61.75	67.64
210	0.65	7.96	81.68	42.16	26.97	25.21	61.38	68.52
508	0.80	6.82	81.12	36.56	27.13	24.63	58.64	68.65

Water/glycol mixture predictions

Also included in Table 7 are the predicted permittivities for the single water/glycol mixture whose dielectric properties were measured at 20 °C. Predictions are lower than measured values by 10 to 15 percent. Clearly, the mixing law exponents that accurately predict soil/glycol/air dielectric response may not apply to this two-component mixture.

What should the mixing law exponents be for the water/glycol mixture? Using the same approach as was applied to soil/glycol/air mixtures, a series of calculations were made for the two-component mixture, the results of which are shown on Figures 20-22 for 45, 210, and 508 MHz, respectively. Again, the measured data (only one point at each frequency) are represented by the plus signs. At 45 MHz, the best fit to this single data point is given by an exponent value of about 2.5; for 210 MHz, it is about 3.0; and for 508 MHz, the exponent needs to be between 3.5 and 4.0. Obviously, the exponents fall outside of the limits set by the simple electrical analogue mixing model.

The most reasonable explanation for the behavior of the water/glycol mixture has to be that the combination of the two components results in a chemical reaction; that one is not dealing with a mixture of two distinct substances and that each retain their individual properties (in this case, permittivities). Rather, the hygroscopic nature of ethylene glycol results in molecules whose effective permittivity is not a weighted sum of the two. The dipole moment of the "particles" of water and glycol is determined by the spatial distribution of mass and charge, and whatever bonding takes place in the combination of the two constituents produces a new substance that is not a simple reflection of its components.

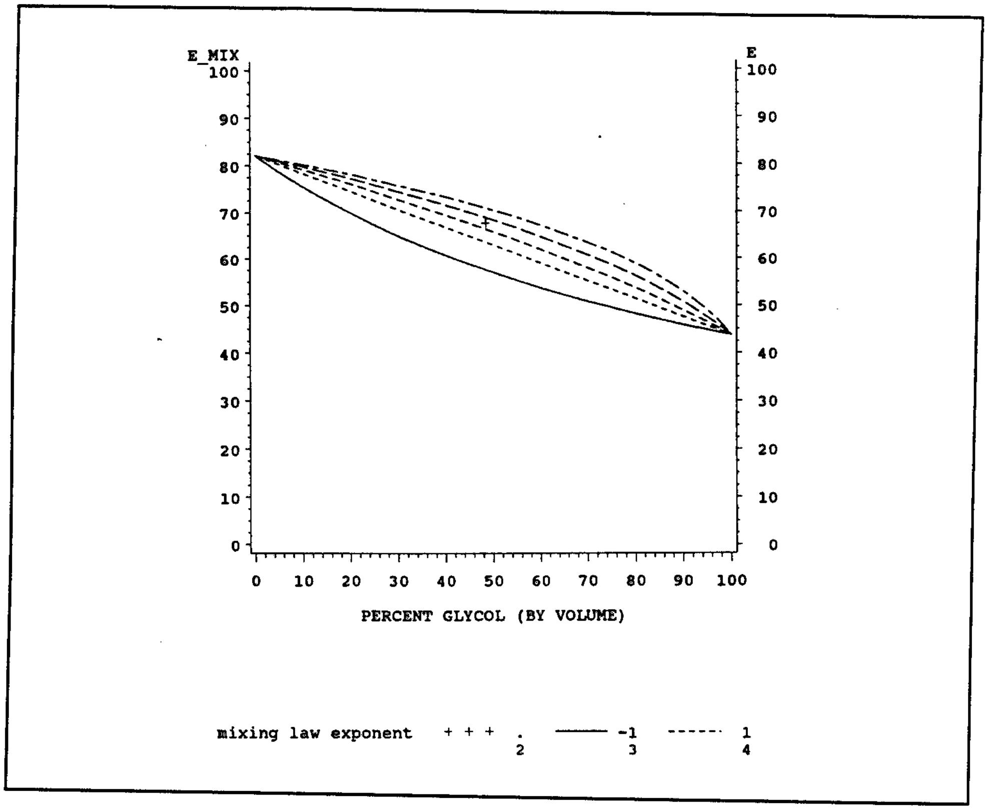


Figure 20. Water/glycol mixture data and model predictions at 45 MHz

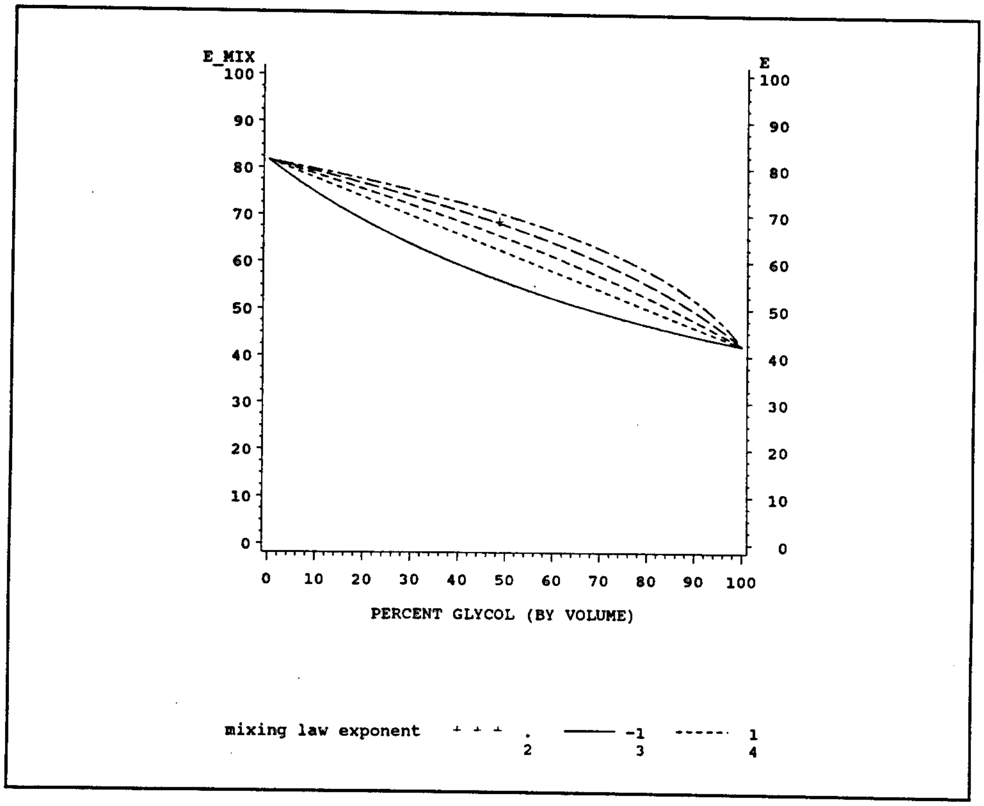


Figure 21. Water/glycol mixture data and model predictions at 210 MHz

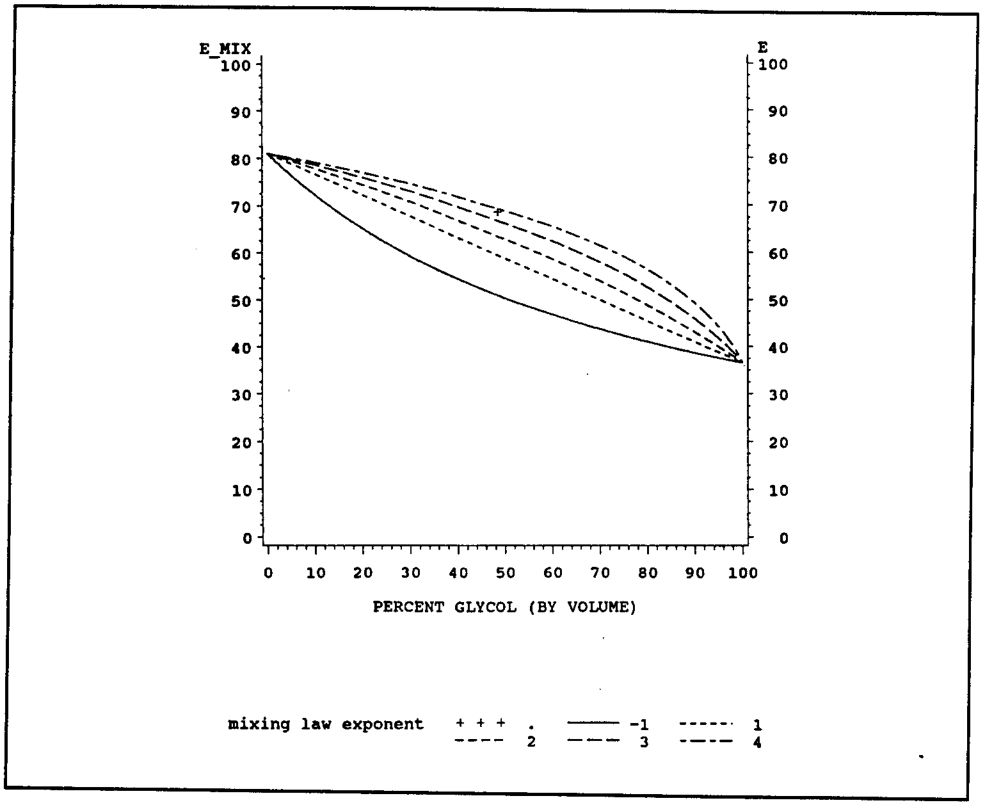


Figure 22. Water/glycol mixture data and model predictions at 508 MHz

The reason that the soil/water/glycol/air mixture behaved in a predictable way was probably due to how the mixture was prepared. Recall from the description of the experimental procedure that the glycol and soil were first mixed together. That gave the glycol dipoles an opportunity to attach themselves to the soil particles just as they had done for the earlier soil/glycol experiments. Water was then added to this mixture. One can only conclude that the water, in this case, does not act as a solvent to the glycol. The best way to test this theory would be to conduct another measurement program in which the soil/water/glycol/air measurements were conducted as before. A second set of measurements would then be conducted by mixing a solution of water and glycol with dry soil. The arguments used above to explain the differences in water/glycol predictions and measurements would then predict lower mixture permittivity values for the second sample. However, time and resources prevent these experiments from being conducted at this date.

Sensor Applications

As for the practical application of this knowledge, one has to ask whether or not a useful sensor can be developed that will be sensitive enough to predict the presence of and/or type of contaminant in a natural subsurface environment. To begin to answer that question, assume that a microwave reflectometer capable of measuring both the real and imaginary part of the complex dielectric constant could be placed in a cone penetrometer as described in the introductory chapter. If one had a good model that related dielectric measurements to the amount and type of contaminant, the chemistry of the soil, and the amount of water in the soil, then it would be possible to measure dielectric properties and predict the degree of contamination.

Clearly, the simple electrical analogue mixing model discussed in this report performed well and reasonably for the one set of soil/contaminant mixture measurements conducted for this study. By virtue of its significant permittivity, ethylene glycol was chosen as the subject of mixture behavior. Any of the other contaminants would have had a significantly smaller impact on the mixture response, because their dielectric properties were not much different from those of the dry soil. There are, however, a number of concerns derived from this study that indicate that a highly sensitive reflectometer that makes use of only the permittivity of the subsurface mixture is not feasible.

First of all, consider the question of sensitivity. For the few data points collected in this study, the deviation of the data from the best fit model is as much as 2 percent by volume. This translates to twenty thousand parts per million. Environmental cleanup standards often deal with acceptable limits of a few parts per million or maybe even a few hundred parts per million. Although not enough data were collected to provide a statistically significant sample from which to accurately calculate standard deviations from the best model fit, these few data points clearly indicate that the sensitivity of such a probe would not be acceptable.

Secondly, there is the question of what influence groundwater would have on the measurements. While the best fit model did a good job of predicting the permittivity of a mixture of soil, water, glycol, and air, it requires that the volume fractions of solid particles, water, and air be known. In other words, the prediction of the volume content of contaminant requires complementary measurements of the in situ moisture content and void ratio.

The most promising application of such a hypothetical sensor appears to be associated with the measurement of the loss term in the dielectric constant. Each pure contaminant that possesses a permanent electric dipole moment has the potential for exhibiting a unique loss spectrum (see the imaginary part of the dielectric constant in Figure 14). If the frequency of peak loss is significantly different from that of naturally occurring water (in the 10- to 100-GHz range), then it might be possible to use a form of microwave spectroscopy to identify certain contaminants. The problem gets suddenly complicated, however, when one throws in the soil matrix (see Figure 8). It is obvious that the frequency of peak loss shifts to the right as the volume fraction of the contaminant decreases in a constant soil matrix. The addition of water to the matrix further complicates the problem by introducing other loss mechanisms at low frequencies that dramatically affects the magnitude of the loss term. Clearly, the only hope for using spectroscopic techniques for these broadband spectra is to be able to measure at least the range of frequencies examined in this report (keep in mind that some of the contaminants studied here did not even show a dielectric loss peak for this band of frequencies, even though they possessed a permanent dipole moment).

On the positive side of the practical sensor question, two comments must be made. One is that, while the results of this study indicate that identifying a particular contaminant and its concentration may be extremely difficult for a sensor operating in the microwave portion of the spectrum, data collected by such a sensor would, in many instances, clearly indicate the presence of something other than just soil and water. This is particularly true in situations where contaminants have the ability to pool either on top of the water table (as in the case of light nonaqueous phase liquids, LNAPLs) or on some impermeable lens within the water table (as in the case of dense nonaqueous phase liquids, DNAPLs). In this regard, a microwave reflectometer or spectrometer would serve to complement the information gathered by any other geophysical sensors contained in the probe.

The second positive observation is that, while broadband spectroscopy may be difficult to interpret, there is still an opportunity to develop a field-based narrow-band microwave spectroscopy device connected to the probe that could, in fact, identify particular substances. Its limitations currently are that it requires a gas sample in near vacuum conditions. Microwave spectroscopic technology is quite mature and highly accurate, but adapting it to field use may be very difficult.

5 Conclusions and Recommendations

Careful measurements of the complex dielectric properties of well-characterized pure contaminants have revealed that the relative behavior of each substance is predictable from its physical properties. In particular, the relative magnitude of permittivity (the real part of the complex dielectric constant) was found to be a function of such properties as specific gravity, relative molecular mass, permanent dipole moment, and the physical temperature of the substance. On the other hand, the resonant frequency or electric dipole relaxation was found to be a function of temperature, dynamic viscosity, relative mass, and the magnitude of the dipole moment. This study did not go as far as to establish the exact form of the relationships that would predict the absolute values of permittivity and resonant frequency, but rather to be able to argue why the magnitude of one substance was different from another and in what direction the difference should be.

Simple mixing models derived from electrical analogues were shown to be successful in predicting the dielectric response (permittivity) of mixtures of a well-characterized soil and one particular contaminant, ethylene glycol. The exponents of the volume-weighted models were found to be a function of frequency, increasing significantly over the 45- to 510-MHz range of frequencies chosen for detailed study. At each frequency, the model provided an excellent prediction of the measured response of a mixture of soil, water, glycol, and air.

The same simple models were not found to be accurate for a mixture of pure water and pure ethylene glycol. The best explanation for this observation is that the mixing of water with the hygroscopic glycol results in a new set of chemical bonds and "particles" having an effective dipole moment and mass distribution that does not fit the assumptions of the electrical analogues. An additional set of measurements were recommended in Chapter 4 that might help confirm this thesis.

Detailed arguments were given to explain why a microwave sensing system that measures only the permittivity of the soil/water/contaminant/air mixture will have little chance of being successful in detecting and identifying small concentrations of particular contaminants. On the other hand, broadband spectroscopic measurements of the loss term of the complex dielectric constant show much more promise in at least identifying substantial concentrations of those contaminants. The practical aspects of developing such a sensor technology are left for a future study.

Other arguments were made to show that a microwave reflectometer in a cone penetrometer platform, while probably not able to detect and identify contaminants at the regulatory level, should be very useful as part of a suite of geophysical sensors that can be used to accurately characterize subsurface conditions, particularly with respect to the water table and to sites where contaminants have pooled above or within the water table.

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13. ABSTRACT *(Maximum 200 words)*

A laboratory measurement program was conducted to explore the fundamental electrical properties of organic contaminants and contaminant/soil mixtures. Complex reflection and transmission coefficients measured by a vector network analyzer system for samples contained in coaxial sample holders were used to generate electrical properties of the pure substances and the mixtures. The frequencies covered by these experiments ranged from 45 MHz to 26.5 GHz, and sample temperatures were held fixed at 10, 20, 30, and 40 °C. Data were reported in the forms of the complex dielectric constant, conductivity, loss tangent, normalized phase velocity, and power attenuation.

Simple volume-weighted mixing models for predicting the real part of the complex dielectric constant (permittivity) were applied successfully to single-frequency data. The rationale behind the development and some of the limitations of mixing models are discussed. The results of this study indicate that permittivity measurements, alone, will not be useful in detecting small concentrations of contaminants in soils. On the other hand, spectroscopic data that cover a frequency range large enough to reveal the dielectric relaxation loss phenomenon that occurs in many organic contaminants may prove to be useful as a detection and/or identification tool.

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