DIELECTRIC PROPERTIES OF BIOLOGICAL MATERIALS: A PHYSICAL-CHEMICAL APPROACH

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of ALI SALEH ALSHAMI find it satisfactory and recommend that it be accepted.

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ABSTRACT

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Dielectric heating of biomaterials was investigated from the physical, chemical, and electrical properties perspectives. Primary focus was on the electrical properties, especially dielectric properties. The dielectric constant (ε') and loss factor (ε") were studied at the molecular level of the materials' composition; primarily water, carbohydrates, and proteins. Effects of components were investigated individually and in combination in aqueous media. Measurements were conducted using an open-ended coaxial probe connected to an impedance analyzer.

Properties of food carbohydrates (starch, sucrose, glucose, and fructose) were investigated over the frequency range 10–1800 MHz at 20–60 ^{o}C, and to 100 ^{o}C for starch solutions. The influences of electrical field frequency (*f*), temperature (T), and concentration (C) on the dielectric constant and loss factor were thoroughly examined and theoretically interpreted. The dielectric constant's response to frequency was fairly

independent from 10 to 1000 MHz, but began a significant and progressive decline at frequencies beyond 1000 MHz.

Influences of protein solutions (ovalbumin, bovine serum albumin, β-lactoglobulin, and lysozyme) were investigated in aqueous media at 450 selected frequencies between 5 MHz and 1800 MHz. All examined proteins exhibited similar dielectric dispersions for the selected concentrations (i.e., 5, 10, 20, 30, 40 and 50 mg/g) and results agreed fairly well with previously published data. Delta-dispersions (δs) between β and γ-dispersions for protein solutions were observed, although at higher relaxation frequencies than those previously published. Contribution of individual proteins to the dielectric loss, and consequently thermal generation in dielectrically heated biomaterials, was investigated and found to have greater effect at low frequencies, especially at 27 MHz. Theoretical calculation of the local dielectric constant (ε') of individual proteins from their amino acid composition resulted in a mean value of 2.70. A derived mixture equation provided results that agreed with experimental data at frequencies close to the industrial microwave frequency (915 MHz).

Dielectric measurements of protein-sugar aqueous mixtures were also conducted in the 10–1800 MHz frequency range. Rayleigh, Böttcher, and Berentsveig mixture models were utilized to predict the mixtures' dielectric constants. Calculated values agreed with the experimental data, except for the three-component mixture result obtained using the Rayleigh model.

TABLE OF CONTENTS

LLIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

BACKGROUND AND RESEARCH STATEMENT

1.1. INTRODUCTION

In a review on the principles and developments of dielectric heating of foodstuffs in *Advances in Food Research*, Dr. Samuel A. Goldblith (1967) wrote, "there still remains a paucity of knowledge on the basic dielectric properties of foodstuffs under a variety of conditions. Such data are necessary and relevant to the problem of judging the optimum frequency for various types of foodstuffs and for different processing operations. These data are necessary not only for indicating the limitations of microwaves but also for indicating other possible uses of this new method of processing."

Four decades later, the paucity of knowledge mentioned remains; little progress has been made in the understanding of biological material responses to an applied electromagnetic (EM) field. Scientists and engineers involved in designing equipment and processes that utilize EM energy at microwave (MW) and radio frequencies (RF) acknowledge that the dielectric properties of treated materials are the principal parameters for coupling the EM energy from the source to the product. Also established is that the amount of energy stored and distributed within a product being dielectrically heated is primarily controlled by its EM properties, especially the dielectric properties (Metaxas and Meredith 1983). The designated industrial, scientific, and medical (ISM) frequencies of the EM spectrum are of particular interest in dielectric heating, which

include four frequency bands used for RF heating centered at 6.78, 13.56, 27.12, and 40.68 MHz, as well as two frequencies commonly used for MW heating, centered at 915 and 2450 MHz (Wig, 2001).

Various research groups and investigators have attempted to construct databases for the dielectric properties for a variety of foods and agri-materials under different temperature and composition conditions. Unfortunately, reported data for the same products vary significantly from one source to another, yet this is not surprising since biological materials are biologically active media. Determining accurate values for the dielectric properties of a particular biomaterial is even more demanding for researchers involved with modeling and simulation of equipment and processes for dielectric heating application. Modelers must perform a large number of dielectric measurements for every case they intend to simulate under a variety of operational conditions. In addition to difficulties associated with the product, complications also frequently arise with measurement techniques and devices. All things considered, the problems with quantifying the dielectric properties of biological materials seem to stem from a lack of understanding of the material behavior as a whole when subjected to an EM field.

The most obvious remedy for this complicated issue is to extend the study of the dielectric behavior of biological materials to their constituents rather than continuing to investigate them as natural complex mixtures. With foods, better insight into dielectric behavior can be gained by studying water, carbohydrates, proteins, fats, and lipids separately. If the dielectric behavior of each of these components and their mixtures is accurately characterized, integrating the results into the overall makeup of the food will

eventually result in mathematical models that can predict desired dielectric properties under various conditions. If successful, an investigator would not need to conduct measurements for every product he/she wishes to study for every process and system parameter.

1.2. RESEARCH STATEMENT AND OBJECTIVES

The primary challenge in developing dielectric heating systems and processes is product heating uniformity. Other reasons given for the lack of success in commercial operations for food sterilization applications are complexity, expense, inability to ensure sterilization of the entire package, lack of suitable packaging materials, and unfavorable economics when compared to prepared frozen foods.

Many techniques have been carried out to improve the uniformity of heating. These include rotating and oscillating the food package, providing an absorbing medium (such as hot water) surrounding the product, equilibrating after heating, and cycling the power Success with these processes is limited due to the tremendous dependence of temperature and its distribution on food dielectric properties and oven factors.

Over the past 50 years researchers have observed that a product's dielectric parameters change dramatically with changes in its physical and thermodynamic properties. The influences of dielectric properties on chemical reaction kinetics have been observed by many researchers in the chemical and food processing technologies

(Gabriel, 1998). Chemat and Esveld (2001) reported an elevation of a product boiling point by 5–40 ^{o}C at saturation pressures in response to an applied EM field.

Despite several decades of effort, what causes these effects and how they are caused on a molecular level remain unclear. The success of studies to formulate analytical and empirical models has been primarily limited to pure substances and binary solutions (Bengtsson 1970, Mudgett 1974, 1975, 1977, Nelson 1984, 1985, Datta et al. 1994, Sun et al. 1995). Therefore, it is proposed here to extend these pioneering efforts to multi-component systems such as food products and multi-component chemical solutions in an effort to add to the existing databases or at least contribute to their expansion for broader application.

The specific objectives of this research are as follows:

1 To investigate the nature of the EM phenomenon and the mechanisms of its application on biological materials at ISM frequencies, especially the MW and RF of the spectrum.

2 To investigate the relations between system thermodynamic and chemical properties and their material dielectric behavior.

3 To establish a physical-chemical basis of dielectric behavior in biological systems as a mean of predicting dielectric properties at various frequencies of interest in dielectric heating processes.

1.3. DIELECTRIC HEATING FUNDAMENTALS

Dielectric heating in food processing includes mainly MW and RF heating, which involves two primary mechanisms: dielectric and ionic. Water in food is often the principal component responsible for dielectric heating. Due to their dipolar nature, water molecules try to follow the electric field associated with EM radiation as it oscillates with very high frequencies to produce heat. The second major mechanism of heating with MW and RF is through the oscillatory migration of ions in foods that generates heat under the influence of oscillating electric fields.

Food shape, volume, surface area, and composition are critical factors in MW heating. These factors can affect the amount and spatial pattern of absorbed energy, leading to effects such as corner and edge overheating, focusing, and resonance. For example, a curved shape can focus MW and produce a higher internal rate of heating than near the surface. Such heating patterns can also change with time. Since the total energy absorbed lags the increase in volume, average temperature rise drops.

Composition has a much greater influence on MW processing than in conventional processing due to its influence on dielectric properties. High salt and moisture contents in particular increase the efficiency of MW absorption, thereby decreasing the depth of penetration. Thus, the interiors of foods with high salt or moisture contents generally do not heat well, reducing microbial destruction. Composition can also change thermal properties such as specific heat, density, and thermal conductivity, and thereby change the magnitude and uniformity of the

temperature rise. For example, the temperature of a low specific heat oil increases at a much faster rate than that of water when compared at the same level of absorbed power.

1.3.1 THE ELECTROMAGNETIC SPECTRUM

By definition, the EM spectrum is the distribution of EM radiation according to energy, frequency, or wavelength. The following table (Table 1.3.1.1) gives approximate wavelengths, frequencies, and energies for selected regions of the EM spectrum (Wig, 2001).

Table. 1.3.1. 1Spectrum of electromagnetic radiation.

Region	**Wavelength (Angstroms)**	**Wavelength (centimeters)**	**Frequency (Hz)**	**Energy (eV)**
Radio	$> 10^{9}$	> 10	$< 3 \times 10^{9}$	$< 10^{-5}$
Microwave	10^{9}–10^{6}	10–0.01	3×10^{9}–3×10^{12}	10^{-5}–0.01
Infrared	10^{6}–7,000	0.01–7×10^{-5}	3×10^{12}–4.3×10^{14}	0.01–2
Visible	7,000–4,000	7×10^{-5}–4×10^{-5}	4.3×10^{14}–7.5×10^{14}	2–3
Ultraviolet	4,000–10	4×10^{-5}–10^{-7}	7.5×10^{14}–3×10^{17}	3–10^{3}
X-Rays	10–0.1	10^{-7}–10^{-9}	3×10^{17}–3×10^{19}	10^{3}–10^{5}
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^{5}$

MW and RF heating refer to the use of EM waves of certain frequencies to generate heat in a material. Typically, MW food processing uses 2,450 and 915 MHz,

and RF uses 13.56, 27.12, and 40.68 MHz. The energy absorption from MW and RF can raise the temperature of a food high enough to inactivate microorganisms for effective pasteurization or sterilization. A number of studies have proven that the thermal effect is the essential contributor to the destruction of microorganisms.

MW and RF heating for pasteurization and sterilization are preferred to conventional heating primarily because they require less time to reach the desired process temperature. This is particularly true for solid and semi-solid foods that depend on the slow thermal diffusion process in conventional heating. They can approach the benefits of high-temperature-short-time (HTST) processing whereby bacterial destruction is achieved, but thermal degradation of the desired components is reduced. This is illustrated in Fig. 1.4.1 in the following section for typical time-temperature histories of MW and conventional heat processes.

MW and RF heating can be more uniform than conventional heating, depending on the particular heating situation; however, heating uniformity is hard to predict. Other advantages of MW and RF heating systems are that they can be turned on or off instantly, are more energy-efficient, and products can be pasteurized after being packaged.

1.4. DIELECTRIC HEATING AS A HIGH-TEMPERATURE-SHORT-TIME-METHOD

It is well known that thermal processes such as pasteurization and sterilization are very important to stabilize foods and assure their microbiological safety, but can also

cause quality degradation. When a thermal process is applied, part of the product's original nutritional and sensorial quality is lost. Although the negative effects of thermal processes cannot be avoided, they can be minimized by optimizing process conditions after identification of the process purpose.

Quality optimization of thermally processed food products is possible due to the temperature dependency of target microorganism thermal degradation kinetics and quality attributes. This is the basis of the HTST principle. In Figure 1.4.1 the bold line corresponds to equivalent time-temperature processing conditions in terms of microbial lethality, indicating that at higher temperatures the quality factors are relatively more thermal-resistant. Therefore, an HTST sterilization regime (UHT treatment), when applicable, results in products with superior quality.

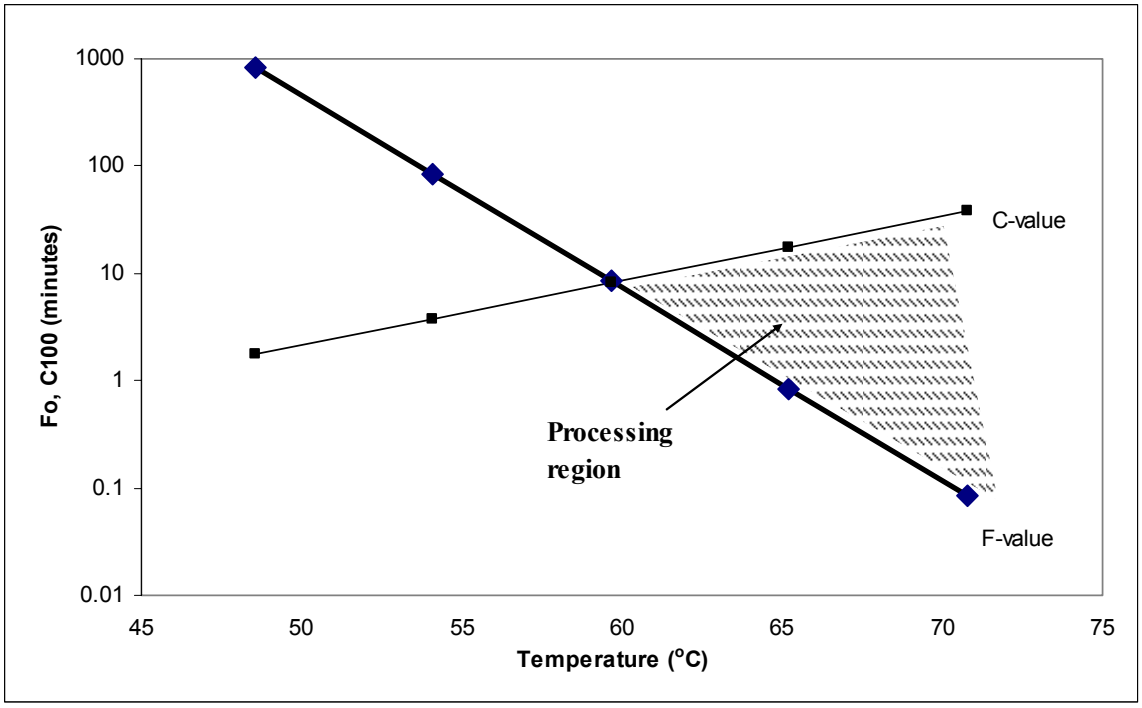

Figure 1.4.1. Graphical representation of the high-temperature-short-time principle.

1.5. MICROBIAL INACTIVATION MECHANISMS IN DIELECTRIC HEATING

As with other thermal processes, the main factors that determine product safety are temperature and processing time (i.e., integrated time-temperature history) (Tang et al. 2000). Some of the critical process factors that affect time-temperature history are moisture, ionic content, field frequency, product parameters (including mass, density, and geometry), specific heat, and the temperature achieved. The spatial distribution of time-temperature history, in turn, changes the distribution of inactivation within a food, thus generally changing the total inactivated population within a given food sample. Such a difference is attributed to the effect of salt in decreasing the penetration of MW, which leads to a lower internal temperature and less destruction in the interior regions, resulting in an overall lower destruction.

In dielectric heating two mechanisms are proposed for inactivation of microorganisms by EM energy (U.S. Food and Drug Administration 2000). The first relies on EM waves to inactivate microorganisms entirely by heat through mechanisms comparable to other biophysical processes induced by heat, such as denaturation of enzymes, proteins, nucleic acids, or other vital components, as well as disruption of membranes. A second proposed mechanism for inactivation by EM energy involves non-thermal effects. The selective heating theory states that solid microorganisms are heated more effectively by EM waves than the surrounding medium and are thus killed more readily. Electroporation is caused when pores form in the membrane of the microorganisms due to electrical potential across the membrane, resulting in leakage. Cell membrane rupture occurs as a result of the voltage drop across the membrane. Another theory states that cell lysis occurs due to coupling of EM energy with critical molecules within the cells, disrupting internal components of the cell.

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CHAPTER TWO

LITERATURE REVIEW

2.1. INTRODUCTION

A synopsis of research activities in the field of dielectric heating of biological materials (e.g., foodstuff) using radio frequency (RF) and microwave (MW) systems is presented to establish the current state of knowledge about dielectric heating technologies, especially for industrial food processing applications. The subsequent two sections detail the essential role dielectric properties of materials play in resolving issues related to heating patterns and uniformity, equipment design, process design, and safety concerns.

2.2. PREVIOUS RESEARCH IN DIELECTRIC HEATING OF BIOMATERIALS

Although research in the field of dielectric heating as applied to biological materials dates back to the early 1940s, serious advancements did not occur until a decade later due to the pioneering work of Von Hippel and his co-workers. Von Hippel's group appears to be the first to provide a sound theoretical basis and interpretations for dielectric heating technological developments. Their work resulted in an important database of dielectric properties on common substances, foodstuffs, and other materials (Von Hippel 1995). Their work on the dielectric behavior of pure water and aqueous salt solutions at various frequencies and temperatures is considered a classic, reliable, and important reference today.

By the late 1970s, analytical chemists became attracted to dielectric heating technology and its effects on chemical reactions and sample preparation. High precision instrumentation was continuously in dire need for homogenous samples at the molecular level in the liquid phase. While there were many advances in analytical instrumentation, techniques for transforming solid samples into homogenous solutions had not progressed with the same fervor. Many chemists were still using 150-year-old mineral acid, beaker dissolution, and Soxhelt extraction methods, which can take hours or days to complete and are susceptible to biases, including the skill of the analyst and contamination of the sample (Kingston and Haswell 1997).

By 1975, domestic MW ovens were used to rapidly heat mixtures of sample and digestion acids to their atmospheric boiling point in an Erlenmeyer flask. This new MW process allowed sample digestions, which used to take several hours with a hot plate, to be completed in less than 30 minutes. It was then when Microwave-Enhanced Chemistry (MEC) made its début as a fast, efficient, and reproducible sample-preparation method. MEC made it possible to heat solutions so efficiently that reaction timescales were dramatically reduced, often from days to minutes, with a level of reaction and process control better than any other heating method.

By the 1980s, researchers were using closed vessels for MW digestion, reaching temperatures above the atmospheric boiling point. Two papers by Ganzler and Salgo (1986) reported the first use of MEC for extracting organic compounds from contaminated soil and plants. They observed that it was possible to increase the temperature of reactions in common organic solvents up to 100 °C above the

conventional boiling point of the solvent. For example, although ethanol has a conventional boiling point of 79 °C, an application of MW dielectric heating in a closed vessel can rapidly lead to temperatures of 164 °C and a pressure of 12 atmospheres (Gabriel 1998). This higher temperature leads to a thousand-fold acceleration of the reaction rate for reactions in typical solvents.

Nevertheless, MEC methods developed to date have been on a trial-and-error basis and contributed little to optimization strategies or researchers' understanding of MW interactions and digestion mechanisms. Over the past 10 years, more than 300 papers were published describing the applications of MW dielectric heating to chemical problems. Much of the work, however, is empirical and qualitative. The theoretical basis of MW dielectric heating remains poorly understood by many chemists and chemical engineers, and although the database of dielectric properties initiated by Von Hippel and extended by others contains significant information about materials and foods, the data for commonly available organic solvents used for chemical reactions are not readily available to the chemical community.

By the early 1970s, researchers began to carry out investigations in an attempt to establish predictive models for the dielectric responses of food materials in an EM field. Using synthetic milk solutions as well as beef and turkey products, Mudgett et al. (1974, 1975) and Sipahioglu et al. (2003) observed that solute-solute and solute-solvent interactions caused a reduction in the dielectric loss factor to levels substantially below those predicted by chemical composition alone. Hence, they concluded that the dielectric

loss factor could not be predicted from a linear, additive model based on composition (Mudgett et al. 1975, Wang and Schmugge 1980).

In 1971 Mudgett and others (1971) reported that the addition of milk salts, which act as mobile charge carriers, depressed the dielectric constant and elevated the dielectric loss in comparison to pure water. They also observed that bound salts and insoluble organic material caused the exclusion of more dielectrically active components from the total volume. In addition, carbohydrates, as studied in alcohol and sugar solutions, exhibited synergistic dielectric loss (i.e., the loss of the mixture was greater than the loss of either the solute or the solvent alone). Roebuck and Goldblith (1972) suggested this was due to hydrogen (H) bonding stabilization that shifted the relaxation time of the free water. They speculated that the charged surfaces of proteins and their complex hydrophobic folding pattern had multiple effects on the dielectric behavior. They also concluded that proteins may simultaneously behave like charged salt particles, carbohydrates with H binding at the surface, and insoluble materials, which would result in volume exclusion. Bengtsson and Risman (1971) proposed that the presence of fats, which have low dielectric activity, cause a dilution of dielectric properties as a result of a decrease in water content.

With the advent of more sophisticated dielectric measurement techniques, qualitative investigations of dielectric properties grew and tangible results were reported for chemical and biological systems. Various research groups described methods to determine the temperature and frequency dependence of the dielectric properties of foods and biomaterials. A few investigations suggested the possibility of correlations for the

dielectric constant and loss factor as a function of frequency, temperature, density, and composition. For example, Seaman and Seals (1991) demonstrated that fruits with similar water contents exhibited similar dielectric behavior. For a group of fresh fruits and vegetables at 2,450 MHz, Nelson (1983) found that the dielectric constant correlated well with moisture content. Nelson (1985a, 1985b, 1991) also developed a series of mathematical predictive models for the dielectric properties of corn, various cereal grains, soybeans, and rice based on frequency, moisture content, and density.

The dielectric properties of various meats, fish, fruits, and vegetables measured by Bengtsson and Risman (1970) showed similar trends of dielectric behavior with temperature and moisture content. However**,** a correlation of the dielectric behavior of foods based on temperature, moisture content, and other compositional components remains plausible. Wang and Wig (2003) measured the dielectric properties of protein gel, liquid protein mixture, and a macaroni and cheese product at 27, 40, 915, and 1,800 MHz frequencies over a wide temperature range (20–121.1 ^{o}C). Their findings demonstrated that as temperature increased, the dielectric constants of whey protein products increased at 27 and 40 MHz, but decreased at 915 and 1,800 MHz. They also found that the dielectric loss factors of whey protein products increased sharply with increasing temperatures at 27 and 40 MHz, but increased mildly at 915 MHz.

A new approach of correlating dielectric properties of biological materials was introduced by Sun et al. (1995), in which they performed statistical analysis of dielectric data for various foods and solutions from published works. Their objective was to provide insight into the contribution of each of the five components (water,

carbohydrates, proteins, fat, and ash) of foods to the overall dielectric behavior. Their findings in relation to the composition dependence of dielectric constants in meats, fruits, and vegetables demonstrated that water alone captures part of the food behavior (high moisture content foods 90, 91, and 96%). They formulated a mathematical model that under-predicted the dielectric properties of meats, with the exception of cooked products, and over-predicted that of fruits and vegetables. They observed that the addition of higher order temperature terms for water and ash or the addition of other components such as protein, carbohydrates, and fat in the formulated model either did not improve the correlation significantly or resulted in singularities in the statistical computations due to the small size of the data set.

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CHAPTER THREE

BASIC THEORY AND FUNDAMENTALS

3.1. INTRODUCTION

A dielectric material's ability to absorb electromagnetic (EM) energy and convert it to heat is dependent on its electrical properties. Among the most significant are the EM, especially the dielectric properties, of the material which describe how materials interact with EM radiation. Natural biological materials absorb only the electric part of the EM field, leaving the magnetic field energy (Ryynänen 1995). In the case of non-ionizing radiation and non-magnetic materials, the electric permittivity (ε_r^*) determines the interaction of EM waves with matter.

The general theory of dielectrics, as of today, is not adequately developed to allow for accurate discrimination of the properties of each component in a heterogeneous mixture apart from its observable macroscopic properties. Earlier efforts succeeded for cases where small amounts of solute with well-defined geometrical and physical properties were dispersed throughout a continuum of a solvent material. Developments in the theory are largely due to the work of Peter Debye in the 1920s, especially for dipoles dispersed in gases or non-polar liquids. A succinct account of the theory was given in his classical book *Polar Molecules* (Debye 1929). In cases of polar liquid solvents, the majority of the reported work is related to inorganic solids dispersed in pure solvents.

3.2. DIELECTRIC CONSTANT AND LOSS FACTOR

Generally the dielectric behavior of a material is described by two parameters, the relative permittivity (dielectric constant, ε_r') and the loss factor (ε_r''). The real component of the permittivity is related to the capacitance of a substance and its ability to store electrical energy; for a vacuum, $\varepsilon_r' = 1$. The absolute permittivity of a vacuum is ε_o, determined by the speed of light (c_o) and the magnetic constant μ_o, which are linked by the equation

$$C_o^2 \mu_o \varepsilon_o = 1 \tag{3.2.1}$$

The numerical value for ε_0 is about 8.854×10^{-12} F/m, while in other media (solid, liquid, and gaseous) the permittivity has higher values and is usually expressed relative to the value in a vacuum:

$$\varepsilon_{abs} = \varepsilon_r' \varepsilon_o \tag{3.2.2}$$

where ε_{abs} = the absolute permittivity of a material, ε_r' = the relative dielectric of a constant, and ε_r'' = the relative dielectric loss factor.

The imaginary component ε_r'' is related to various absorption mechanisms of energy dissipation, is always positive, and usually much smaller than ε_r', especially for higher frequencies (i.e., > 40 MHz). The substance is lossless if $\varepsilon_r'' = 0$ (Wig, 2001). The ratio of ε_r'' to ε_r' is called the dielectric loss tangent, where $\tan \delta = \varepsilon_r'' / \varepsilon_r'$. The

equivalent conductivity σ of a material can be computed from its loss factor ε_r" and temporal frequency f (or its radial frequency ω) according to:

$$\varepsilon''_{r_\sigma} = \frac{\sigma}{2\pi f \varepsilon_o} \tag{3.2.3}$$

Dielectric theory is based on the classical relations of the electrostatic field. The most relevant are Maxwell's formulations, in which the dielectric constant (ε') of a material is defined in terms of the applied (or induced) electrical field E and electrical displacement (electric flux density) D, yielding the following equation:

$$D = \varepsilon' E \tag{3.2.4}$$

Because D and E have direction as well as magnitude, they are vector quantities. Since the present work deals with homogenous and isotropic dielectrics, ε is independent of direction and is to be regarded as a scalar quantity. The simplest interpretation of Eq. 3.2.4 is that the magnitude of the electrical displacement (i.e., flux density) to an applied energy gradient (i.e., electric field density) is reduced by a constant that is related to the nature of the material that is coupling them. One should note the similarity of this formulation to Fick's law of mass diffusion, Fourier's law of heat diffusion, and Newton's law of momentum diffusion, which makes it yet another phenomenological law of transport.

From the electrostatics theory standpoint, the most direct and least complex route to explain Eq. 3.2.4 is by observing its resemblance to the definition of capacitance (C):

$$q = CV \tag{3.2.5}$$

where q is the charge on the capacitor plate and V is the voltage difference between the plates. Furthermore, this is not just a mathematical similarity, but a physical similarity as well; C and ε' are both properties of a material placed in an electric field (i.e., $C_{\text{with a dielectric}} = \varepsilon' C_{\text{without a dielectric}}$). Since $C_{\text{with a dielectric}}$ is always larger than $C_{\text{without a dielectric}}$, the value of ε' must always be greater than one. Thus, by measuring the capacitance with and without the dielectric material, a ratio of the capacitance should give the dielectric constant.

The existence of a dielectric constant different from unity (value for free space) is explained classically by the polarization (P) of the particles comprising the medium. The polarization, which is defined as the average dipole moment (μ) per unit volume, can be accounted for by the following expression (Von Hippel 1995):

$$D = \varepsilon_o E + P \tag{3.2.6}$$

From Eqs. 3.2.4 and 3.2.6,

$$P = \left(\varepsilon' - \varepsilon_o\right) E \text{ or } P = \left(\varepsilon_r' - 1\right) \varepsilon_o E \tag{3.2.7}$$

where ε_r' is the dielectric constant of a material relative to the vacuum dielectric constant.

Aside from the simplicity this definition of P provides for formulating electrical equations, it also provides a link between the microscopic model of atomic and molecular dipoles and a macroscopic description of neutral dielectrics. The average dipole moment,

a statistical parameter commonly quantified in classical physics using Boltzmann's distribution, is often thought of as resulting from the additive action of N elementary dipole moments:

$$P = N\overline{\mu} \tag{3.2.8}$$

Molecular polarization occurs in the presence of an electric field so that it increases with the size of the field. The average dipole moment thus formed is a function of the magnitude of the dielectric field that acts on the material:

$$\overline{\mu} = \alpha E_{local} \tag{3.2.9}$$

The constant of proportionality α, often referred to as polarizability, measures the electrical flexibility of the particles. In this sense, when a material is acted upon by an external electric field, the electrical structure of the material at the atomic level is expected to exhibit a response in the form of an alignment with the field. The extent of the alignment is quantified using the polarization mechanism. The alignment contribution to the material's total polarizability comes from the induced dipoles as a result of the external field application and the alignment of the permanent dipoles:

$$\alpha = \alpha_{ind} + \alpha_{perm} \tag{3.2.10}$$

The induced polarizability can further be divided into contributions due to electronic polarization (α_e), which results from the displacement of the negatively charged electronic cloud surrounding the positively charged nucleus, and atomic polarization (α_a), from the electronegativity difference of bonded atoms from different

types of molecules. These three mechanisms of polarization, characterized by electronic polarizability (α_e), atomic polarizability (α_a), and permanent dipole polarizability(α_d), are due to charges locally bound in atoms, molecules, or the structures of solids and liquids. Another contribution not often considered in studies of fluid dielectrics is interfacial polarization (α_i), which arises due to migration of charges to the boundaries separating the composition of the considered matter. However, since this is a theoretical treatment where the material is assumed to be a perfect dielectric (free from charge carriers), interfacial contribution will not be accounted for. The total polarizability of a dielectric material, therefore, may be written as the sum of three terms:

$$\alpha = \alpha_e + \alpha_a + \alpha_d \tag{3.2.11}$$

Now that the molecular parameters (μ, N, and α) of a dielectric are linked to the macroscopically measured ε, what remains is characterizing the applied electric field E. Up to this point the polarizability α was assumed to be a real quantity. Although true for static field, in alternating fields a phase shift most often occurs between the applied field and resulting reorientation (polarization); thus α becomes complex and Eq. 3.2.7 has to be replaced by

$$P = \left(\varepsilon_r^* - 1\right)\varepsilon_o E \tag{3.2.12}$$

The preceding discussion of polarizability mechanisms facilitates the following interpretation and analyses of applied electric fields. Since the total polarizibility is a summation of contributions from two sources (induced and permanent dipoles), the electrical field that caused these polarizations must also comes from two sources: 1)

polarization due to the externally applied field ($E_{external}$), and 2) polarization due to the induced field internally within the dielectric ($E_{internal}$). Hence, we obtain

$$E_{local} = E_{external} + E_{internal} \tag{3.2.13}$$

Since our objective is to find a relationship between the polarizability of a biomolecule immersed in an aqueous solution and the bulk dielectric constant, it is necessary to know the magnitude of the field that actually influences the individual molecules and how much they will be polarized, which in turn affects the value of the dielectric constant. Only a brief overview of the relevant equations will be provided here; interested individuals should consult the book *Dielectrics and Waves* by Von Hippel (1995) for extensive analysis of the physical model and relevant dielectric mathematical formulations.

The physicist H. A. Lorentz was the first to calculate E_{local}, and the results bear his name. His model involves a dielectric subjected to the action of an external uniform electric field. He then selected a specific point within the dielectric and constructed an imaginary sphere surrounding this point. According to Lorentz, the electric field at this point is a summation of three separate contributions: 1) the original applied field to the entire medium (i.e., field induced by the polarization of the molecules outside the sphere), 2) the induced field due to the electrodes polarization, and 3) the field due to the polarization of the molecules inside the sphere. The latter contribution is often ignored based on the assumption that an elementary particle is neural and without a permanent dipole. Lorentz showed that the field due to the second contribution is

$$E_{\text{int}ernal} = \frac{P}{3\varepsilon_o} = \frac{E}{3}(\varepsilon' - 1) \tag{3.2.14}$$

Substituting Eq. 3.2.14 into Eq. 3.2.13 and assuming that the external field $E_{external}$ equals the original applied field E yields

$$E_{local} = E + \frac{P}{3\varepsilon_o} = \frac{E}{3}(\varepsilon' + 2) \tag{3.2.15}$$

From Eqs. 3.2.4, 3.2.6, 3.2.9, and 3.2.15, the following is obtained:

$$\frac{(\varepsilon_r^{'} - 1)}{\left(\varepsilon_r^{'} + 2\right)} = \frac{N\alpha}{3\varepsilon_o} \tag{3.2.16}$$

where N is the Loschmidt number of molecules per cubic meter. By replacing the dielectric constant with their counterparts (see Eq. 3.2.12), we arrive at the general formulation commonly known as the Clausius-Mossotti-Lorentz-Lorenz equation:

$$\frac{(\varepsilon_r^{*} - 1)}{\left(\varepsilon_r^{*} + 2\right)} = \frac{\rho N_o \alpha}{3M\varepsilon_o} \tag{3.2.17}$$

where N_o is Avogadro's number (6.023×10^{23}), ρ is the density in (kg/m^3), and M is the molecular weight. Equation 3.2.17 is only an approximation but has provided satisfactory results for gases and liquids with low dielectric constants. For liquids with a high dielectric constant (i.e., water) and strong molecular interactions, Eq. 3.2.17 serves only as a guide, especially in the analysis of experimental data; it is used here to calculate the dielectric constant of protein molecules dispersed in water, and results are reported in Ch. 4.

3.3. POWER DENSITY AND PENETRATION DEPTH

When biological materials are subjected to an EM field at MW frequencies, dipolar relaxation generally dominates, whereby molecules (typically water) absorb energy during the process of repeated reversal of their polarization. At even higher frequencies, relaxation of individual atoms can play a role in dielectric heating. At lower frequencies, however, gross electron conductivity begins to play a greater role in dissipating EM fields. This effect is very slight for pure water, which has a DC conductivity of about 0.55 μS/cm at 25°C, but a pronounced loss at MW frequencies. More conductive materials, such as those containing salts dissolved in water, can have significant low-frequency dissipation. In general, when relaxation effects are discounted, the loss factor of a material is related to its DC conductivity through the following equation:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon_r'' \tag{3.3.1}$$

The rate of heating can be expressed by the power equation:

$$P_v = 2\pi f \varepsilon_o \varepsilon'' E^2 \tag{3.3.2}$$

where P_v = energy developed per unit volume (W/m^3), f = frequency (Hz), and E = the electric field strength inside the load (V/m), determined by the dielectric properties, load geometry , and oven configuration. Such complexity makes this equation generally impractical (Ryynänen 1995).

To gain better practical understanding of dielectric properties, a penetration depth is calculated. Theoretically, the penetration depth (d_p, or power penetration depth) is defined as the depth below a large plane surface of a substance at which the power density of a perpendicularly impinging, forward-propagating plane EM wave has decayed by 1/e from the surface value (1/e = 37%) (Decareau and Mudgett 1985). If tan δ is smaller than about 0.5, the following formula gives 97–100% of the correct value:

$$d_p = \frac{\lambda_o \sqrt{\varepsilon'}}{2\pi\varepsilon''} \tag{3.3.3}$$

where λ_o is the free space wavelength. The absorbed power density near the surface of an infinite inhomogeneous slab is, accordingly, approximately proportional to ε_r" when ε_r' does not vary much.

3.4. WAVE IMPEDANCE AND POWER REFLECTION

Transmission properties, which are related to the dielectric and thermal properties of a medium, determine its distribution of energy. Since ε_r' reduces the speed of propagation, the wavelength in a dielectric medium is shorter than in free space. This change in wavelength leads to a reflection at the interface between two media with different ε'. The reflection phenomena can be analyzed in terms of characteristic wave impedance (η) (Metaxas 1983) as follows:

$$\eta = \frac{\eta_o}{\sqrt{\varepsilon}} \tag{3.4.1}$$

where η_o is the wave impedance of free space (almost 3.77 ohms).

The reflection and transmission at a plane boundary are primarily related to $\sqrt{\varepsilon}$, and the principal determining factor for the magnitude of the reflection is from the real permittivity ε_r' of the material. Errors due to neglecting ε_r'' are less than 5% for virtually all foods (Ryynänen 1995).

Characteristic impedance is important when different materials are heated simultaneously. The characteristic impedance for the average food is about 50 ohms. The change in characteristic impedances (the dielectric mismatch) at the food surface results in reflection of about 50% of the MW power falling on the surface. Most of this energy is reflected back to the food via metal cavity walls. For frozen food, the impedance matching is better, often resulting in higher power utilization for thawing than for heating (Mudgett 1986).

3.5. DIPOLE MOEMENTS AND ELECTROMAGNETIC FIELD INTERACTIONS

The concept of the electric dipole and its response to an applied EM field is essential for understanding the mechanism of dielectric heating within a biological material. It also provides a basis for many molecular phenomena and allows fairly simple models to be constructed to explain those phenomena. Significant information can be acquired about the macroscopic, chemical, and physical properties of a dielectric material based on the presence or absence of a dipole moment. In fact, it has been customary for scientists to divide materials into two general categories: polar and non-

polar. Polar materials are composed of submicroscopic dipoles (i.e., individual molecules possessing a permanent dipole moment in which the center of the positive charge is separated from the negative charge), while non-polar materials are those whose molecules possess no permanent dipole moment unless they are in the presence of an electric field.

The dipole moment (μ) is defined as a vector whose magnitude is given by its total positive or negative charge (q) multiplied by the separation distance (*l*):

$$\mu = lq \tag{3.5.1}$$

and whose direction is represented by the direction from the negative to the positive charge. The SI unit of a dipole moment is that of a proton and electron separated by a distance of 2.38 nm, which is called the *Debye* (D) in honor of Peter Debye.

Dipoles can not only set up an electric field within a dielectric material, but also be influenced by external electric fields. When a dipole is placed in an electric field, uniform or non-uniform, the positive end will tend to move in the direction of the field and the negative end in the opposite direction, resulting in a force that acts on the dipole to cause a rotation about the center. The magnitude of the force is given by

$$F = qE \tag{3.5.2}$$

But since there is no net charge on the dipole, E is constant and the net force acting on the dipole is zero; hence, no translational motion of the dipole. Exact calculation of the

molecule dipole moments from which the dielectric properties are derived is an advanced exercise in quantum mechanics, and will not be attempted in this work.

The importance of the dipole moment concept for dielectric property calculations is twofold: 1) a quantitative description of the time taken by the dipoles to return to their random orientation once the external field is removed, and 2) a tool to mathematically evaluate Maxwell's equation (see Eq. 3.2.4) in terms of the material's structural properties rather than the applied electric field and flux. The time the dipolar molecules take to return to their random orientation is called the relaxation time (τ), and its evaluation is essential for characterizing the material's overall dispersion region. This is the region where the actual energy conversion, from electrical to thermal, takes place and its magnitude determines the amount of power dissipation and heat generation.

3.6. DIELECTRIC PROPERTIES AND FREQUENCY

In a static electric field (zero frequency), the dielectric constant is generally at its maximum and the dielectric loss at its minimum. At very high frequencies, both the dielectric constant and loss are at their minimum values (close to zero). As far as dielectric heating is concerned, the magnitude of the dielectric loss is most important; the higher the loss, the more heat is generated. Although only a few frequencies are designated for industrial applications (ISM frequencies), attempts should be made to identify the optimum frequency for a particular application. For food processing in particular, a choice must be made when selecting a MW or RF oven for commercial processing. For MW, one can chose a unit operating at 2,450 MHz or 915 MHz; for RF

units the choice is between 13.65 MHz, 27.12 MHz, or 40.6 MHz. Selecting the appropriate device with the appropriate frequency should be based on many factors (food type, size, and geometry; processing time, etc.), with the most important being the response of the food and its constituents to the field frequency.

From a dielectric heating perspective, foods can be divided into two primary categories based on their moisture content: high-moisture foods and low-moisture foods. In processing high-moisture content foods, devices operating at MW frequencies (915 and 2,450 MHz) are the most appropriate choice. This is primarily due to the nature of the interactions between the food constituents and field frequency, in which water interactions with the field significantly dominate all other interactions. Accordingly, the majority of the heat generation results from the rotational mechanism of the permanent dipoles of water molecules. This effect can be accounted for approximately using the well-known Debye dispersion equations for the dielectric constant (Eq. 3.6.1) and loss factor (Eq. 3.6.2):

$$\varepsilon' = \frac{\left(\varepsilon_s - \varepsilon_\infty\right)}{1+\omega^2\tau^2} + \varepsilon_\infty \tag{3.6.1}$$

$$\varepsilon'' = \frac{\left(\varepsilon_s - \varepsilon_\infty\right)\left(\varepsilon\tau\right)}{1+\omega^2\tau^2} \tag{3.6.2}$$

where $\tau = \frac{1}{2\pi f}$, ε_s is the static field dielectric constant (≈ 78.5), and ε_∞ is the dielectric constant at very high frequencies (≈ 4.5). Again, the values obtained using the above two equations are only an approximation, and their use should be limited to crude calculations

of the required power dissipation and/or simulation purposes. Accurate values for the dielectric properties may be obtained for foods with high water content if account is made for the amount of water displaced (bound) by the content solids due to its unavailability for interacting with the applied fields.

For low-moisture foods, devices operating at low RF frequencies (13.6, 27.12, and 40.6 MHz) are more suitable than MW systems. This is because at low frequencies, other dielectric mechanisms dominate and heat generation due to water molecule rotation becomes less significant when compared to the amount of heat generated from the rotation of other macromolecules and electrolytes within the food product. Consequently, the readily available Debye equations are no longer adequate for estimating the magnitude of the dielectric properties and related design and process parameters (power dissipation, penetration depth, and processing time). Efforts must then be made to account for contributions from each constituent in the food product in order to yield the correct values for the dielectric constant and loss factor. The current study is a preliminary attempt to perform this task, for which results will benefit both low frequency and high frequency processing.

3.7. DIELECTRIC PROPERTIES AND TEMPERATURE

The thermophysical behavior of biological materials in an EM field is still one of the major issues yet to be characterized before dielectric heating is deemed the method of choice for food processing, especially dielectric pasteurization and sterilization. This is simply due to the fact that uneven heating is still encountered in all forms of dielectric

heating (i.e., RF and MW) under various conditions and at unpredictable locations and time-frames in the process. Cold spots and run-away heating are among the most challenging issues that need to be investigated and resolved before dielectric heating systems are deemed safe for processing foods or any perishable products.

The underlying premise of uneven heating with MW and RF lies in the material's inability to dissipate and/or transport the generated thermal energy at the same rate as the absorbed EM energy. The rate of power absorption in dielectric heating is generally described (Decareau and Mudgett 1985) by

$$\dot{P} = \omega \varepsilon_o \varepsilon'' E^2 \tag{3.7.1}$$

where P is the power per unit volume of dielectric, ω is the angular frequency, ε_o is the vacuum dielectric constant, ε" is the dielectric loss, E is the electric field. Furthermore, the generated heat within the product is also subject to conventional mechanisms of heat transfer by internal conduction, surface convection, and moisture evaporation, which are in turn mediated by the thermal and transport properties of the product. These physical properties are also functions of temperature, and thus vary with time during the heating period.

Experimental data for the dielectric constant of water has shown that a linear relationship can be described (Gabler 1978) by

$$\varepsilon' = a - bT + cT^2 - dT^3 \tag{3.7.3}$$

where a = 87.74, b = 0.4008, c =7.398 x 10^{-4}, and d = 1.410 x 10^{-6}. For other liquids, the relationship between the dielectric constant and temperature can be expressed as

$$\varepsilon' = Be^{LT} \tag{3.7.4}$$

where B and L are constants depending on the liquid. With the formulas just mentioned, the dielectric constant can be approximately calculated for liquid dielectrics for any dielectric for which the formulas are valid. However, caution must be exercised, for the dielectric constant and loss factors are continuously changing depending on the physical situation, and temperature is one of those factors influencing this change.

3.8. DIELECRIC PROPERTIES NAD ELECTROLYTES

Electrolytes are an integral component of any food system, whether in its natural form or industrially processed. It is also common for food scientists and biochemists to rely heavily on solutions with significant salt content as solvents for macromolecules and constituents of food formulations. In this study, where the primary objective is the characterization of the dielectric behavior of biological molecules, electrolyte content in the examined samples and their influence on the overall dielectric behavior of the solution is at issue. The aim here is not to describe the nature of the interactions between the electrolytes molecules and applied EM field, but rather to assess the extent of their influence on the experimental results.

Two opposite effects on the dielectric constant of solutions due to the presence of electrolytes have been observed: 1) at low concentrations, the solution's ε' decreases with

increasing electrolyte concentrations; and 2) at large electrolyte concentrations, the solution's ε' increases (Gabriel et al. 1998). Since the current study deals with solutions that are relatively pure (i.e., contain only traces of electrolyte impurities), discussion will be limited to the low concentration condition. For high concentrations, the most accepted explanation is that as electrolyte content increases, negative and positive ions form dipoles that align with the external field, thus increasing the solution's overall dielectric constant (Gabler 1978). Similar effect is expected for the ε", in which ionic dipoles relax before the smaller water molecules, thus increasing the bulk ε", especially at high frequencies (i.e., MW frequencies).

For small concentrations, although the situation is not entirely clear, it is generally believed that when a salt dissolves in water, it dissociates to form two ions. Since these ions are in an aqueous environment, the dipolar water molecules adjacent to the ions align with the applied field, resulting in a primary hydration layer around the ions. Several researchers have proposed detailed models for the hydration layer structure, including its geometry and dimension (Hasted 1972, Mudgett et al. 1977, Von Hippel 1995). Due to the intensity of the applied field, the aligned water molecules are held strongly in place, rendering them unavailable for alternating alignment with the externally applied field. Because the water molecules are unable to contribute to the total dipolar alignment, the ε' is less than that for pure water. This effect was observed during the investigation of dielectric properties of protein solutions, as reported in Chs. 4 and 6.

3.9. DIELECTRIC PROPERTIES MEASURMENT

Dielectric measurements are generally application-specific, and since each application has different requirements and specifications, a large and growing number of methods exist. For foods, dielectric heating equipment operates at a single frequency, and thus it is tempting to measure the dielectric properties at the specific frequency of interest. This, however, would not work since the heating mechanism is dependent on the relaxation process rather than resonance, and thus characterizing the dielectric properties must be performed over the entire relaxation region. For biological materials, the dispersion region generally covers at least two orders of magnitude, while for heterogeneous systems such as food, dispersion is much wider. It is thus evident that measurements need to be conducted over as broad a frequency band as possible for accurate determination of the dielectric properties and adequate characterization of the dispersions of interest. A practical limitation is encountered when considering the entire length of the EM spectrum, when segmenting the spectra into sub-regions becomes inevitable.

The most common division of the spectra is into low-frequency and high-frequency regions. For the low end of the spectrum, bridge techniques are used, usually the parallel plate method. In theory, bridge techniques can be suitable for measurements up to 300 MHz; practical measurements show that the best results are obtained from 1–300 MHz. Examples of commercial parallel-plate dielectric property fixtures are the Agilent HP16451B Test Fixture (Agilent Technologies, Palo Alto, CA) and the Agilent HP16452A Liquid Test Fixture. Neither fixture is rated for use above 30 MHz. For the

high frequency region, transmission lines are employed; such techniques are subdivided into coaxial lines and wave guides. The frequency range for the coaxial probe method in practice is from around 50 MHz to approximately 12 GHz; above this to just below 100 GHz, waveguides are employed. For a complete description of the theory and methodology for both techniques, readers are advised to consult works such those by Von Hippel (1995), Athey et al. (1982), Stuchly et al. (1982), and Nyshadham et al. (1992). In the current study, the open-ended coaxial probe was chosen for experimental measurements for the following reasons: 1) it allows simple sample measurement and data analysis, 2) the instrumentation is commercially available, and 3) dielectric properties can be obtained over a wide frequency range in a single measurement and with adequate accuracy for thermal calculations (Engelder and Buffler 1991).

The open-ended coaxial probe method is a measurement technique using a cut-off section of a co-axial EM transmission line. The Material is measured by placing the probe to a flat face of a solid or immersing it into a liquid for complete contact. The EM fields at the probe's end fringe into the material and change as they come into contact with the specimen (Fig. 3.9.2).

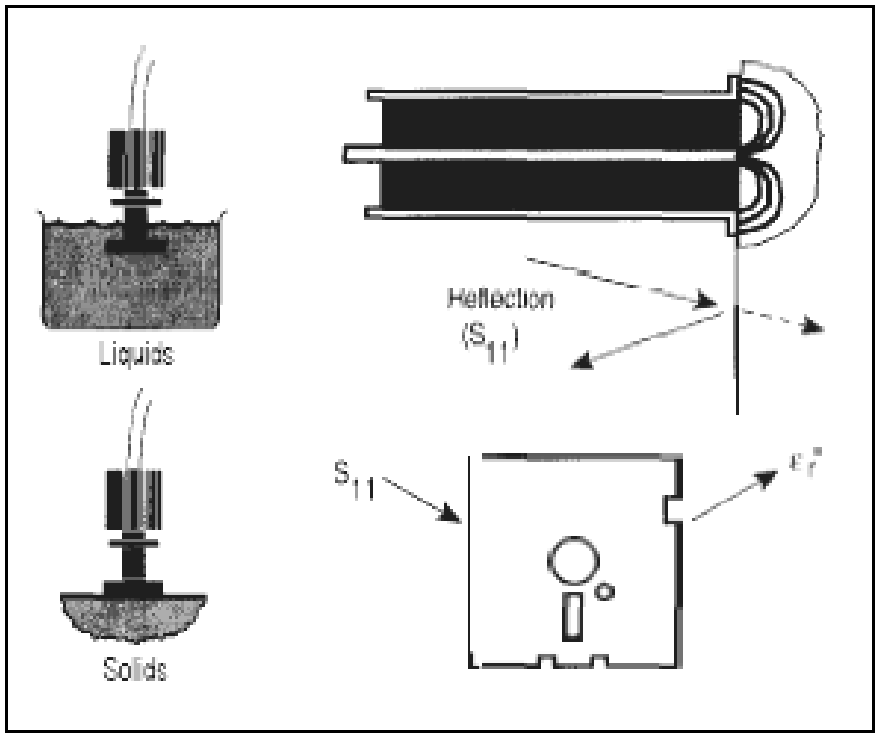

Figure 3.9.1. Open-ended coaxial probe method (HP application note 1217-1).

The parameters (amplitude and phase) of incident and reflected signals are detected by the Automatic Network Analyzer (ANA) or Impedance Analyzer. The reflected signal (S_{11}) parameter is then measured and related to the complex relative permittivity (ε_r^*). A simplified schematic of the measurement procedure is presented in Fig. 3.9.3.

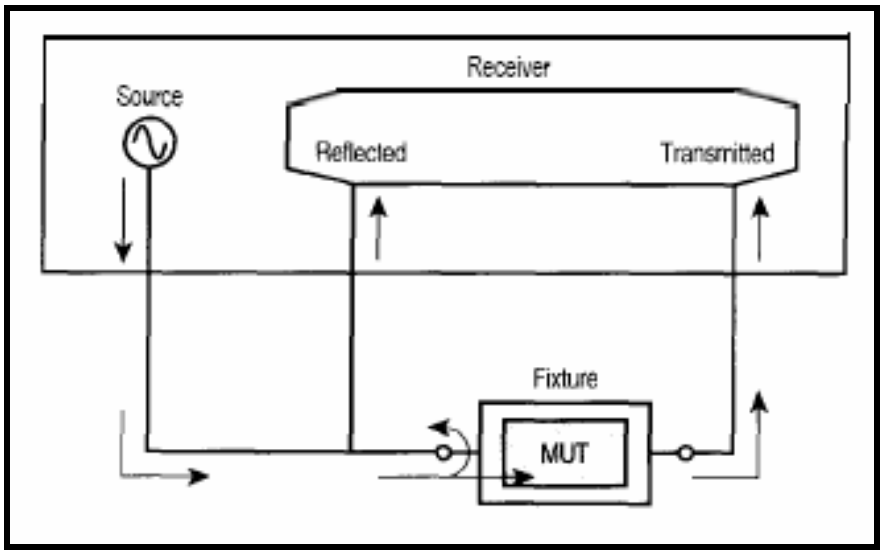

Figure 3.9.2. Simplified measurement apparatus.

The complex dielectric permittivity is determined according to the reflected coefficient $\left(\Gamma = \Gamma' - j\Gamma''\right)$ as follows (Komarov and Tang 2005):

$$\varepsilon' = \left(A_e f\right)^{-1}\left\{\frac{-2\Gamma''}{\left(1+\Gamma'\right)^2 + \Gamma''^2}\right\} \; ; \; \varepsilon'' = \left(A_e f\right)^{-1}\left\{\frac{1-\Gamma'^2-\Gamma''^2}{\left(1+\Gamma'\right)^2 + \Gamma''^2}\right\} \tag{3.9.1}$$

where A_e is the empirical coefficient dependent on characteristic impedance of the probe and sample size. Errors due to reflections and transmission line discontinuities are minimized by performing a calibration procedure prior to every measurement batch. This procedure is generally accomplished using three standard terminations: 1) open, 2) short, and 3) load (50 Ω). The actual reflection coefficient differs from the reflection coefficient measured using ANA $\left(\Gamma_m\right)$:

$$\Gamma = \frac{\Gamma_m - a_{11}}{a_{22}(\Gamma_m - a_{11}) + a_{12}} \tag{3.9.2}$$

where a_{11} is the directivity error, a_{12} is the frequency response error, and a_{22} is the source match error. Given the propagation constant (λ) and distance from the connector to the probe head (z), a_{ij} can be calculated in terms of S-parameters of the connector:

$$a_{11} = S_{11};\ a_{12} = S_{12}S_{21}e^{-2\gamma z};\ a_{22} = S_{22}e^{-2\gamma z} \tag{3.9.3}$$

Open-ended coaxial method is one of the most popular techniques for liquid or soft solid sample measurements of broadband MW and RF and very high temperatures (up to 1,200^{o}C); it has reliable accuracy in the range of 50 MHz to 20 GHz. However, it is not suitable for measuring materials with low dielectric properties (plastics, oils, etc.).

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CHAPTER FOUR

DIELECTRIC MECHANISM ANALYSIS OF FOOD CARBOHYDRATES

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4.1. ABSTRACT

The dielectric mechanism of food carbohydrate solutions (starch, sucrose, glucose, and fructose) was characterized over the frequency range 10 –1,800 MHz at 20–100 ^{o}C. The influences of field frequency (*f*), temperature (T), and concentration (C) on the dielectric constant (ε') and loss factor (ε") were examined and theoretically interpreted. The ε' response to frequency was fairly independent between 10 MHz and 1,000 MHz, but began a notable decline beyond 1,000 MHz. This behavior was interpreted in terms of the viscous effect and formation/breaking of the water's H bond network. Also, the ε' exhibited a gradual decrease with increasing medium temperature, which was attributed to the molecular thermal agitations due to temperature increases that always resulted in disorienting the dipoles and consequently decreasing the ε'. Increasing carbohydrate concentrations resulted in depressing the ε' for all frequencies in the selected range of the spectrum in agreement with the H-bonding-sites concentration hypothesis.

Keywords: Dielectric mechanism, Food carbohydrate solutions, Starch, Sucrose, Glucose, Fructose, Dielectric constant, Loss factor, Dielectric heating

4.2. IINTRODUCTION

Electromagnetic (EM) processing of foods at the radio frequency (RF) and microwave (MW) frequencies of the spectra presents an attractive alternative to conventional thermal (i.e., retorting) methods. Conventional treatments involve transporting energy from the source to the material via two primary mechanisms: conduction and convection, in which heat is transferred from the exterior surfaces into the interior, resulting in a severely damaged peripheral layer and compromising the overall quality of the end product, especially in solid and semi-solid foods (Tang et al. 2001). EM heating technology, on the other hand, generates heat internally throughout a product's volume simultaneously due to the interaction of the EM wave with the material constituents at the molecular level. Since molecules at the interior of the product interact with the applied energy at the same time as those at the surface, heating time is significantly reduced and heating uniformity considerably improved compared to conventional heating. This direct interaction provides the extra benefit of microbial safety to food products when considering the lethal effect on microorganisms resulting from the interactions with EM waves at the cellular level (Mudgett 1985). Additional benefits of EM radiation of biological materials include high energy efficiency, high energy densities, heating independent of the product and medium thermal conductivity, and reduced production floor-space requirements. However, before EM energy completely replaces conventional retorting methods, issues related to the presence of cold spots, edge heating, and run-away heating must first be resolved. Among the fundamental parameters responsible for the majority of the mentioned disadvantages are

the electrical properties of the food product that is to be dielectrically heated, especially the dielectric parameters.

Dielectric properties are the principal parameters responsible for coupling and distributing EM energy into and throughout a product during dielectric heating (Mudgett 1986); namely, the dielectric constant (ε') and dielectric loss factor (ε"). The dielectric constant (ε') measures the ability of a material to store electrical energy, whereas the loss factor (ε") measures the stored energy that dissipates as heat within the product. Quantifying and measuring these parameters is therefore essential for successful application and implementation of developments to this technology to treat foods and other biological materials. Accurate determination of ε' and ε" is not only necessary for determining the magnitude of heat generation and spatial distribution, but also for better design and modeling of MW cavities and RF applicators (Zhang et al. 2001).

Although studies of dielectric properties of biological materials at the molecular level date back to the early 1930s (Grant et al. 1978), this initial work did not deal with the heating effects resulting from subjecting such materials to EM energy. In fact, most studies conducted prior to the 1970s on biological molecules in an EM field focused on finding ways to eliminate or at least minimize the heat generation within the treated product. It was not until the early 1970s, after the advent of domestic MW ovens, that investigators began to look into the possibilities of utilizing and maximizing the generated heat within products for heating and cooking (Von Hippel 1995;, Gabriel et al. 1998). This is primarily due to the basic premise of dielectric heating, which sates that the amount of electrical energy converted into thermal energy in an EM field is directly

proportional to the electric field strength and field frequency, and the constant of proportionality is the relative dielectric loss factor. This principal is mathematically described by the following expression:

$$P_{av} = 2\pi\varepsilon_o f\varepsilon'' E^2 \tag{4.2.1}$$

or, using the equivalent conductivity:

$$P_{av} = \sigma E^2 \tag{4.2.2}$$

where P_{av} is the average power dissipation per unit volume (Watt/m^3), f is the field frequency i(Hz), σ is the equivalent conductivity (S/m), and E is the electric field intensity (V/m). E is considered to be homogenous throughout the sample volume.

From Eq. 4.2.1, one can see that delivering the required amount of thermal energy to a product involves two device parameters (f and E) and one material parameter (ε"). Additionally, E is also established as a function of the material dielectric constant (ε') (Von Hippel 1995). Therefore, designing an EM device capable of providing the specified amount of power requires a precise knowledge of the involved parameters. E and f are input parameters, generally specified by the designer, and controlled externally via the electrical circuitry of the system by f at the generator and E by the separating distance of parallel plate applicators in the case of RF ovens or magnetrons/klystrons for MW ovens. This capability of controlling input parameters is not, however, feasible with the material's dielectric properties.

Another essential parameter for dielectric heating of biological materials that requires accurate determination of the material's dielectric properties is the EM wave penetration depth into the material (Wig 2001). Food product designers must determine product thickness for this parameter a priori. The penetration depth (d_p) of a material, also known as the skin depth or attenuation distance, is a parameter that describes the distance an incident EM wave can penetrate beneath the surface of a material before its electric field intensity is diminished by a factor of 1/e, to about 37% of its amplitude at the surface. It is given by

$$d_p = \frac{c}{2\pi f \sqrt{\varepsilon_r'}\left\{\frac{1}{2}\left[\sqrt{1+\left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2}-1\right]\right\}^{\frac{1}{2}}} \tag{4.2.3}$$

where c is the speed of light in a vacuum, or 2.99792458×10^8 m/s.

It is evident from this formula that determination of ε' and ε" is critical for computing the required thickness of the material to be dielectrically treated. It should be noted here that d_p is one of the primary factors responsible for exploring utilization of EM at the RF band (e.g., 27.12 MHz) and the lower range of the MW band (e.g., 915 MHz) of the spectrum for industrial processing due to their much longer wave length that results in deeper wave penetration.

Dielectric properties are constitutive of a material and thus vary significantly from one material to another; they are a strong function of frequency, temperature, and composition (Zhao et al. 2000). After researchers began investigating the dielectric

properties of biological properties for heating purposes, investigations were generally carried out by experimenting with bulk mixtures of complicated composition. Foods were subjected to direct measurements of their dielectric properties, with very little success. Inconsistent, unpredictable, and irreproducible experimental data were obtained for a variety of food products. This inconsistency was due in part to the lack of understanding of the fundamentals underlying the dielectric behavior of food components in an EM field, and was not resolved until the early 1970s when efforts shifted from studying the dielectric properties of foods as mixtures to the behavior of their principal components.

This study of the dielectric properties of food carbohydrates intends to provide an analysis and quantification of the dielectric mechanisms and their responses to processing parameters such as temperature, concentration, and frequency in the MW and RF ranges of the EM spectrum.

4.3. MATERIALS AND METHODS

The measurement system used in this study consisted of an Agilent 4291B impedance analyzer (Agilent Technologies, Palo Alto, CA), an open-ended coaxial probe (Hewlett-Packard 85070B), a custom-built test cell, and a VWR Model 1157 programmable circulator (VWR Science Products, West Chester, PA). The impedance analyzer was connected through an IEEE-488 (GPIB) bus to a desktop personal computer, which was used with custom-designed software DMS 85070 (Innovative Measurements Solutions) to control the impedance analyzer and log the measured data. The impedance analyzer was calibrated by warming (by turning on the power switch) for at least 30 min before

measurements were conducted per the recommendations of the manufacturer, then using the 4219B calibration kit. The kit included four calibration standards: an open, a short, a 50X load, and a low-loss capacitor. The testing probe was calibrated using an 85070B dielectric probe kit that included a short circuit (a gold-plated precision shorting block), an open circuit (air), and a known load (pure water at 25°C).

After calibration, samples were placed into a custom-built temperature-controlled test cell. The probe was then inserted into the loaded test cell and kept in contact with the sample during the measurement. The test cell was constructed of two coaxial sections of 1 in. and 1.5 in. OD 304 stainless steel sanitary tubing welded to a 1 in. sanitary ferrule at each end to serve as the sample holder and water jacket. The dielectric probe was installed through a solid sanitary end cap and sealed with an o-ring. The probe and end cap mated with the top end of the water-jacketed sample holder, sealed with a gasket and held in place using a sanitary clamp. A thermocouple port was mounted through the bottom sanitary end cap covering the other end of the sample holder. A stainless steel spring and a stainless steel piston provided constant pressure on the sample, maintaining close contact between the sample and the probe tip through the entire measurement. A thin 1.02 mm rigid stainless steel thermocouple probe passed through a pressure-tight gland in the thermocouple port, through the center of a spring and piston, and into the center of the sample to determine its temperature. For a complete description of the experimental test-cell is given in Wang et al. (2003).

Dielectric property measurements were performed on starch (National 1215®, a white to off-white powder, pregelatinized, unmodified corn with approximately 8%

moisture and 6 pH, procured by National Starch & Chemical, New Jersey), glucose, fructose, and sucrose (Sigma-Aldrich Chemicals; St. Louis, MO; see Table 4.3.1 for relevant material properties) solutions. Aqueous solutions of 10% , 20% , and 30% (wt/wt) concentration levels were prepared by dissolving required amounts of carbohydrates in distilled and double-deionized (DDI) water (ionic conductivity ≈ 0.23 μS/cm) constantly stirred (for starch samples, blending was accomplished using a Stomacher 400 circulator [Seward, 110 VOLTS, t20 AMP 5x20 mm SLO-BLO FUSES]) and continuously heated using a standard hot-plate heater (for starch the WSU cell was used). The probe was cleaned with DDI water and wiped dry by dry paper towel before and after each measurement. Measurements were conducted in triplicate every 10°C from 20–80°C. Sample temperatures were verified using a digital thermometer (Barnatt 115, Mode l600–1020, Barington, IL). The probe system was calibrated with a standard calibration procedure (air-short-triple-deionized water).

Table 4.3.1. Relevant physical and chemical molecular parameters used in this study.

Compound	**Number of (-OH) groups**	**Polarizability $(\alpha)^1/10^{-24}$ cm^{-3}**	**Dipole moment $(\mu)^2$ Debye**	**Dielectric Constant $(\varepsilon)^3$**	**Molecular weight (Mw)**
Water	1	1.494†	1.8	78–82	18
D-Glucose	5	12.0	3.8	72–69	180
D-Fructose	4	11.9	3.2	74–70	180
D-sucrose	8	22.5	8.3	74–70	342
Starch	>>	NA	NA	72–65	>9,000

[1]Data from Wang et al. 1998
[2]Data from Fuchs and Kaatze 2002
[3]Dielectric constant range from 10–1,800 MHz at 20°C
†From International Association for the Properties of Water and Steam 2001

4.4. RESULTS AND DISCUSSION

4.4.1 FREQUENCY INFLUENCE

Figures 4.4.1.1 and 4.4.1.2 present an example of the dielectric mechanism exhibited by the examined carbohydrates as a function of field frequency at 20 ^{o}C and 20% solute content. Figure 4.4.1.1 represents the results for the dielectric constant (ε') and Figure 4.4.1.2 the behavior of the dielectric loss (ε'') compared to the dielectric mechanism of pure water. Figure 4.4.1.1 shows that for all investigated carbohydrates, the ε' is fairly independent of field frequency from 10 MHz up to 1,000 MHz; beyond 1,000 MHz, a significant decline is clearly observed. This behavior can be safely interpreted in terms of the physicochemical properties of the solutions: namely, the viscous effect and formation/breaking of the water's H bonds network. Figure 4.4.1.2 shows the dielectric loss mechanism as a function of frequency for the investigated molecules, which was typical for all investigated carbohydrates. A more detailed analysis of the ε'' behavior is provided in the section related to temperature and concentration effects.

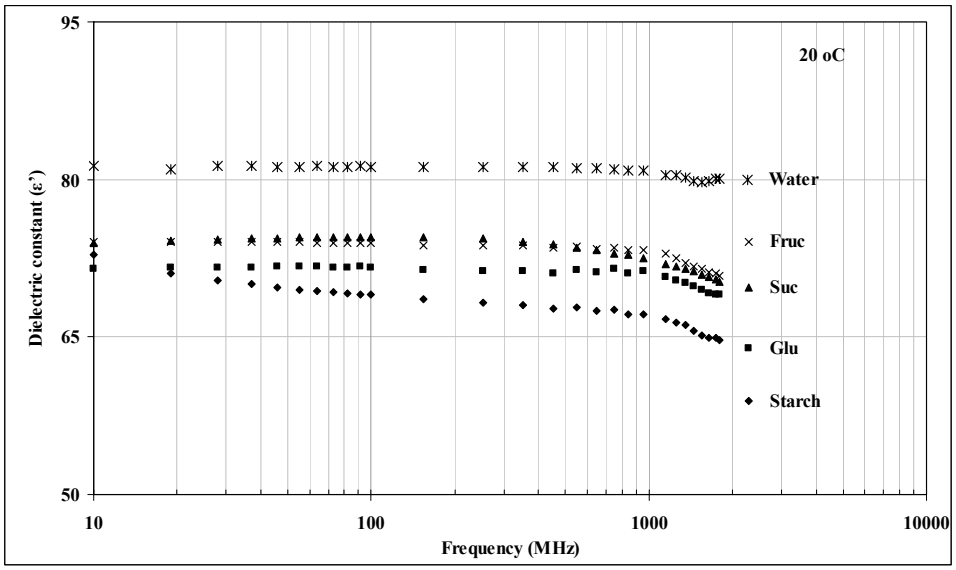

Figure 4.4.1.1. Dielectric constant (ε') spectra of glucose, sucrose, fructose, and starch (20%, w/w; 20°C) as a function of frequency in the RF and lower MW ranges of the spectrum.

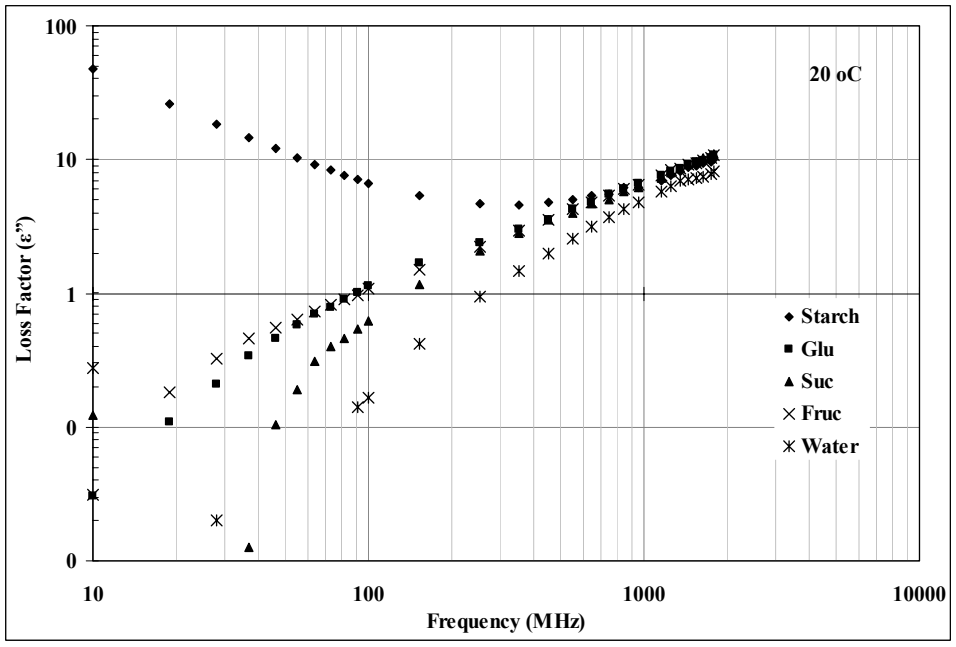

Figure 4.4.1.2 Dielectric loss spectroscopy of common food carbohydrates (starch, glucose, sucrose, and fructose) at 20% (wt/wt) concentrations, and double-deionized-water at 20°C.

The viscous effect, first proposed by Oncley (1930), explains the sudden drop in ε' at higher frequencies where the orienting molecular torque is no longer sufficient to completely overcome the resisting viscous forces causing the molecules to cease reorienting with the applied AC field, resulting in what is commonly known as "dielectric relaxation." Dielectric relaxation is generally described in terms of relaxation time (τ), which is the time it takes the molecules to return to their initial random orientation prior to the application of an AC field. The viscous force effect on the dielectric relaxation is primarily a function of solute concentration and molecular size and structure. Viscosity increases with concentration, consequently resulting in larger retarding forces for molecular reorientation, which in turn causes a decrease in dielectric relaxation times as previously demonstrated by Haggis et al. (1952). Similarly, as molecular size and conformation increases, lower dielectric relaxation times are realized (South and Grant 1974, Pethig 1979). This interpretation is clearly supported by the behavior depicted in Fig. 4.4.1.1, in which pure water has the lowest viscosity and smallest molecular size resulting in the highest ε', whereas the starch solutions have the highest viscosity and largest molecular size and consequently the lowest ε'.

The continuous forming and breaking of the H bonds in the water network also affect the ability of the molecules to keep pace with the AC up to the point where conditions are no longer favorable for this process to be sustained (Fuchs and Kaatze 2001). Thus, when the H bond network no longer provides suitable conditions for molecular reorientation, dielectric relaxation occurs. If frequency is further increased beyond the relaxation frequency (f_R), EM energy is no longer absorbed and molecular orientation ensues, resulting in electrical energy conversion to thermal energy that

ultimately dissipates as heat. This effect is apparent in the exhibited behavior of the investigated carbohydrates and water depicted in Fig. 4.4.1.1. In terms of the H bond network, water forms a 100% -H bond network, which is slightly weaker than any other –H bonds formed. Thus, breaking/making of the -H bonds process in water is faster, enabling molecules to follow the AC field and resulting in high ε' (Fig. 4.4.1.1).

With regard to carbohydrate solutions, fructose molecules have the lowest number of –OH groups (four), which when present as a monomer in water forms (i.e., stabilizes) fewer –H bonds, resulting in more available water to interact with the AC field. The dielectric behavior of carbohydrates is thus second to water in terms of its capability to keep up with the alternating field and resulting in the highest ε' after water. Also, it is useful to point out that fructose, in the context of this study, comes second to water in terms of its dipole moment (≈ 3.2) and Mw (≈ 112). In other words, fructose is the second largest molecule after water. This fact contributes to the dielectric mechanism of fructose solutions in two different ways: 1) its small size provides it with the flexibility to overcome the induced viscous effect, resulting in easier rotation with the AC field; and 2) its relatively small dipole moment provides the molecule with the needed compactness to facilitate reorientation with the AC field.

Similar interpretations can be applied to other carbohydrates, with few exceptions related to the behavior of sucrose and starch solutions. The similarities and variations in the dielectric behavior of both the sucrose and starch compared to fructose and glucose is interesting inasmuch the previous two compounds are polymers of the latter two. Sucrose is a dimer of glucose and fructose, whereas starch is a polymer of glucose

molecules. The dielectric similarities are evident in their overall response to the fluctuating field frequency exhibited by the dielectric constant, as shown in Figure 4.4.1.1. The variation, however, relates to the behavior of the sucrose solution in which it was expected have lower ε' values than the mono-sugars since it has a higher dipole moment (≈ 8.3), higher Mw (≈ 254), higher numbers of –OH groups (= 8), and larger molecular structure. This anomaly was unexpected and may be attributed to either measurement or experimental error. Nevertheless, this behavior needs to be further investigated over wider concentration and frequency ranges.

4.4.2 TEMPERATURE INFLUENCE

From a thermal analysis point of view, it is expected that most other responses by a biosystem to an applied EM field will be masked or significantly dominated by the response of the water molecules making up the system. It is therefore safe to interpret the experimental results due to temperature variations in terms of the water (bound and free) molecules' responses only, especially since the samples here are aqueous solutions. The classical work of John Kirkwood (1939) on polar liquids appears to be the first to provide a theoretical treatment and accurate explanation of the thermal effect on water molecules placed in an EM field. Kirkwood's analysis resulted in a mathematical expression in which ε' is directly proportional to the molecular polarization of the material, which is in turn inversely proportional to the system temperature. This is consistent with the molecular thermodynamic model of dielectrics, which explains that as the system temperature increases, random thermal motion and agitations tend to increasingly disorient the alignment of the dipoles, hence decreasing ε'.

The experimental results of this study agree with the above theoretical analysis and interpretations. Figures 4.4.2.1, 4.4.2.2, and 4.4.3.3 exhibit a gradual decrease in ε' with increasing temperature for all examined carbohydrates. The sucrose solution's response to temperature variations, however, demonstrated an interesting behavior in which their decrements with increasing temperature were minimal or almost constant at both the RF (27.12 MHz) and MW (915 MHz) frequencies. This is again unexpected, and its behavior as a disaccharide should fall between the mono- and polysaccharide solutions in accordance with the hypothesis of the H bonding sites concentration presented by Haggis et al. (1952), Roebuck et al. (1972), and Fuchs and Kaatze (2001). According to this hypothesis, the higher the number of –H bonding sites (i.e., -OH group in organic molecules), the larger the number of water molecules that would bind, making them less available for alignment with the applied EM field, and hence lowering the ε' of the overall aqueous solution. Having almost twice the number of –OH groups than glucose and fructose, sucrose solutions are expected to have a lower ε' that should also decrease with increasing temperature due to destabilization of the –H bonding network. No further explanation can be offered here for the dielectric behavior of sucrose in aqueous solutions, further examination is highly recommended.

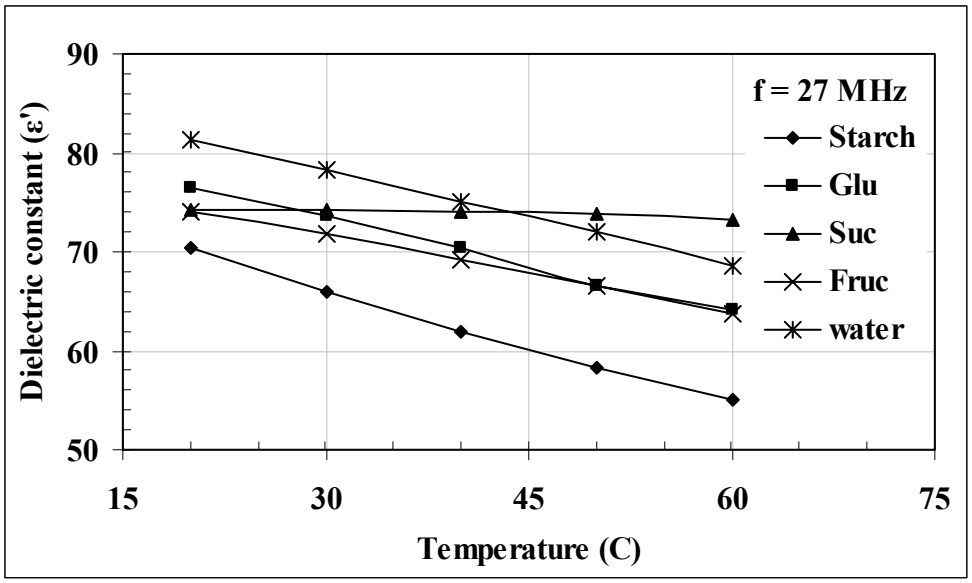

Figure 4.4.2.1 Dielectric constant (ε') response to temperature variations at RF frequency (27.12 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

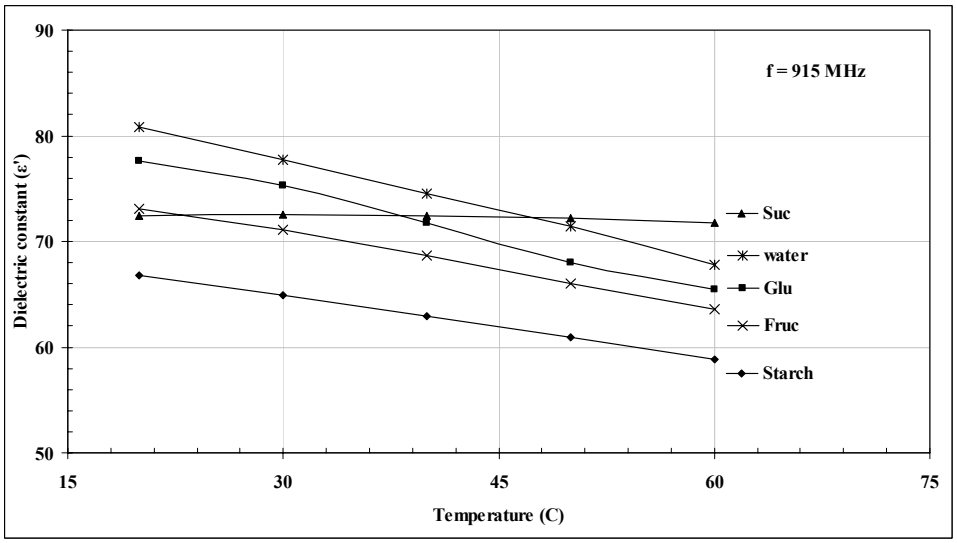

Figure 4.4.2.2. Dielectric constant (ε') response to temperature variations at MW frequency (915 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

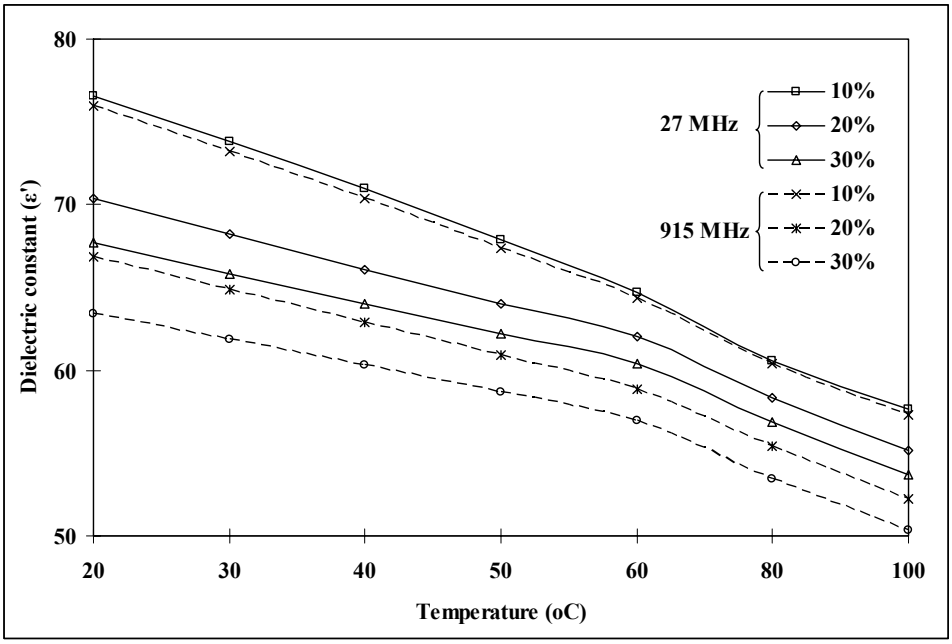

Figure 4.4.2.3. Temperature and concentration effects on the dielectric constant (ε') at the RF (27.12) and MW frequencies (915 MHz) of the EM spectrum for starch solutions.

The deviation of sucrose behavior from the molecular model described above in response to increasing temperature follows previous deviations for other biological materials previously reported in the literature. For example, Nelson and Bartley (2002), Feng and Tang (1998), and Wang et al. (2003) all reported an increase of ε' with increasing temperature for RF and MW frequencies alike. Although all agreed that low moisture contents of the examined products seemed to be the primary factor, they did not support their argument with an analytical justification. A likely explanation for the rise of ε' with temperature in the authors' results is that products (i.e., aqueous mixtures) with major constituents having relaxation times much lower than water will most likely exhibit an increase of ε' with increasing temperature. In other words, the dielectric molecular theory applies only to the left side of the spectroscopic dispersion curve, in correspondence with static dielectric conditions. The behavior of molecules past the

critical relaxation frequency (f_R) is exactly the opposite to that prior to f_R with regard to elevation of the system's temperature. This behavior is further amplified by the response of the dielectric loss (ε'') to temperature variations.

The molecular dispersion region, generally represented by a bell-shaped curve when ε'' is plotted as a function of frequency, normally shifts to higher frequencies as the temperature is increased (Tang et al. 2001). In addition to reduction of the relaxation time, this shift commonly causes a reduced ε''. Reduction of ε'' at the dispersion region is always accompanied by a reduction of ε'; hence, increasing temperature causes an increase in ε'. This justifies results where ε' exhibits an elevation with increasing system temperature. It is, however, valid for mixtures that are free from impurities and electrolytes. The presence of ionic substances, as is the case with the starch solutions used in this study, significantly mask the ε'' response to temperature variations, as shown in Figs. 4.4.2.4 and 4.4.2.5. The significant elevation of ε'' in both figures is clearly a consequence of ionic loss, which is generally dominant at lower frequencies, especially for food systems.

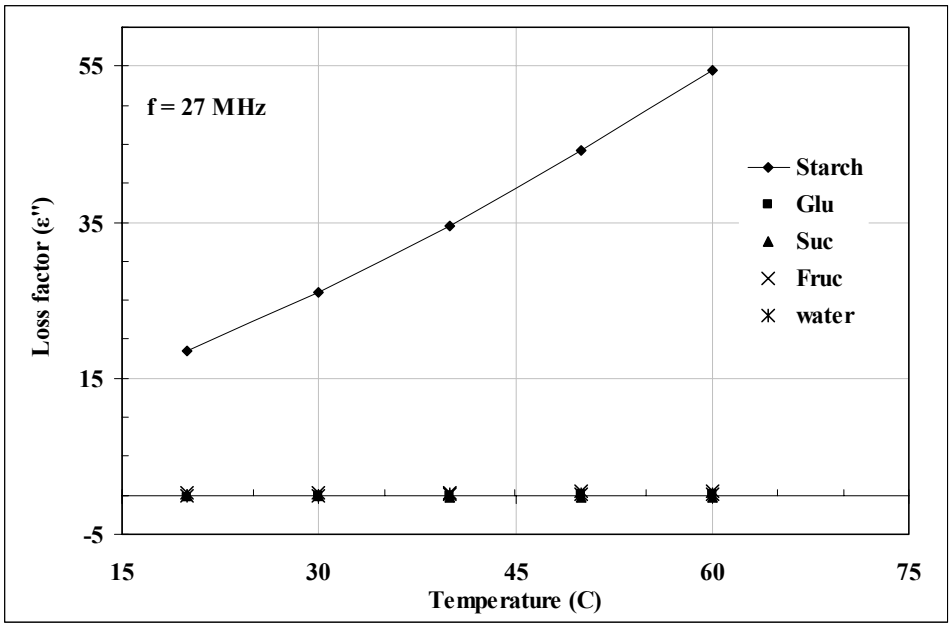

Figure 4.4.2.4. Dielectric loss (ε'') response to temperature variations at RF frequency (27.12 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

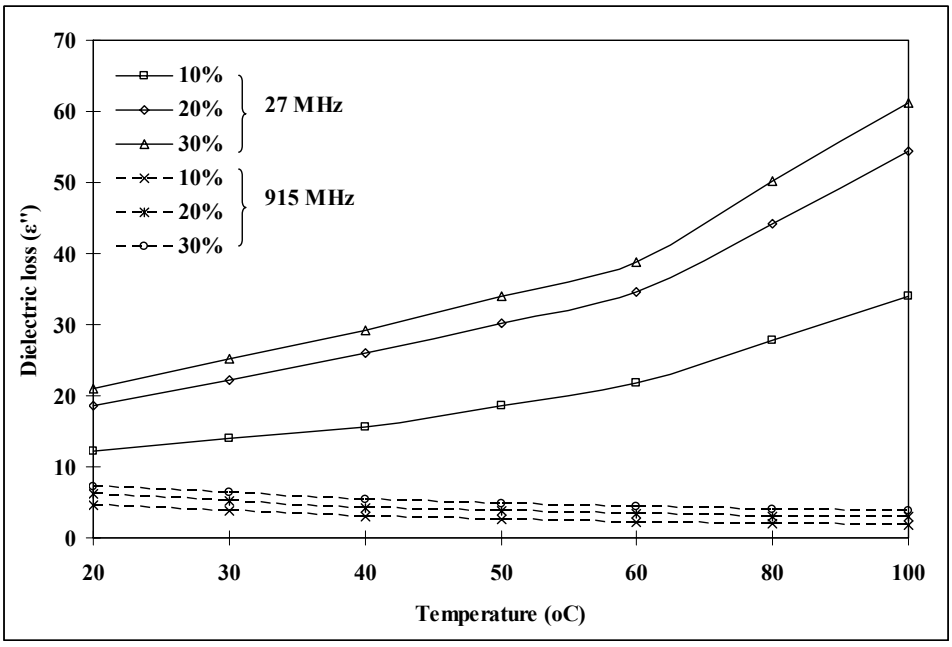

Figure 4.4.2.5. Temperature and concentration effects on dielectric loss (ε'') at the RF (27.12) and MW frequencies (915 MHz) of the EM spectrum for starch solutions.

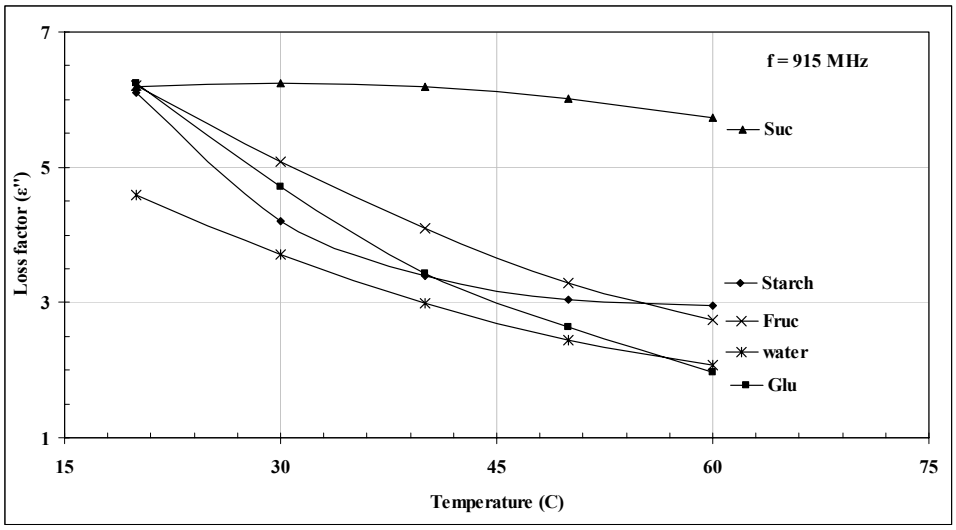

Figure 4.4.2.6. Dielectric loss (ε'') response to temperature variations at MW frequency (915 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

4.4.3 CONCENTRATION INFLUENCE

Increasing carbohydrate concentrations resulted in depressing the ε' for all frequencies in the selected range of the spectrum (Figs. 4.4.3.1 and 4.4.3.2). This is again consistent with the –H bonding sites concentration hypothesis discussed previously in the temperature section. Higher concentrations of organic molecules in aqueous solutions result in increasing the –OH active sites for –H bond formation with the neighboring water molecules. This in turn lowers the number of available dipoles of the major mixture constituent (i.e., water) for interacting with the applied electrical field. The magnitude of the reduction in ε' is a function of the overall concentration of the dipoles within the mixture. If both solute and solvent molecules are dipolar in nature, then the reduction will be less than if only the solvent molecules are.

Carbohydrates are, in general, considered dielectrically inactive when in aqueous solutions compared to dielectrically active water molecules (Mudgett 1985). This is

particularly true from a dielectric heating point of view where the dielectric loss is the major factor considered. Purified carbohydrates (i.e., ions-free) do not contribute significantly to the overall dielectric loss of mixtures, especially at the RF frequencies shown in Figs. 4.4.3.1 and 4.4.3.2. The minor increase in ε'' shown in Fig. 4.4.3.4 is most likely the contribution of the surrounding water molecules (free and bound) rather than the carbohydrate molecules themselves. Also, it should be noted again that the increase in ε" for starch solutions depicted in Fig. 4.4.3.3 is due primarily to the presence of the ionic residues generally associated with starch granules (Baldwin et al. 1997). Most common food components such as starch, proteins, and fats release significant amounts of ions when dissolved in food systems, causing considerable change in the dielectric properties of the system, especially in the RF range of the spectrum (Gunasekaran 2002).

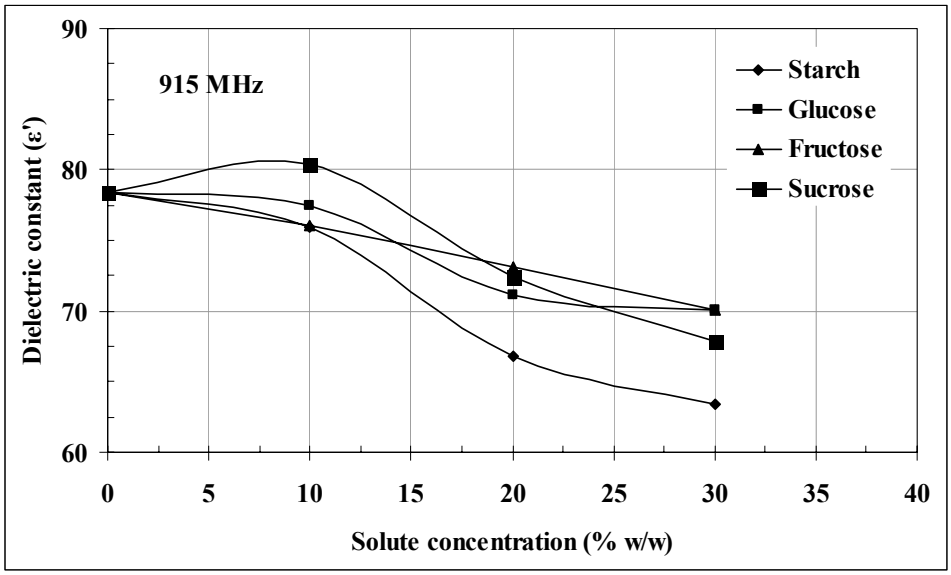

Figure 4.4.3.1. Dielectric constant (ε') response to concentration variations at MW frequency (915 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

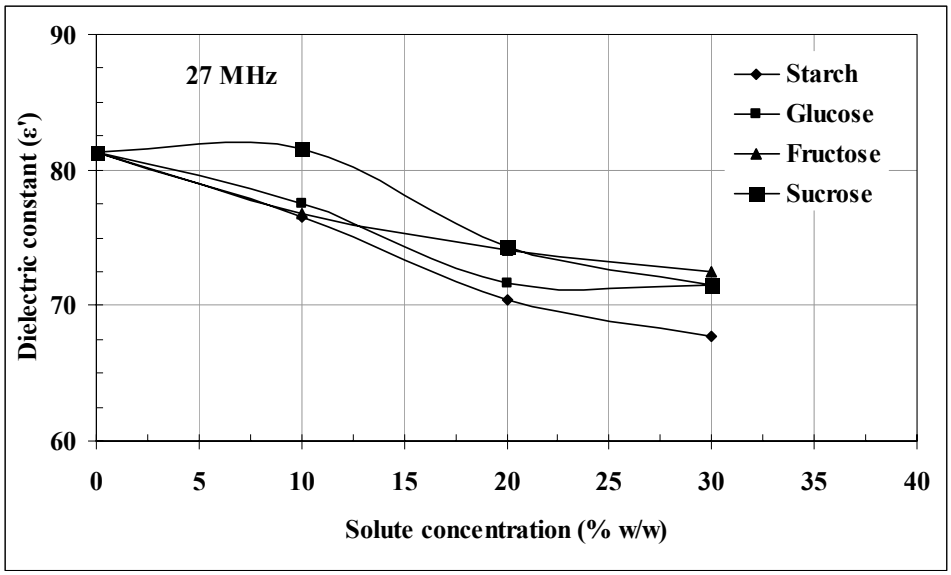

Figure 4.4.3.2. Dielectric constant (ε') response to concentration variations at RF frequency (27.12 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

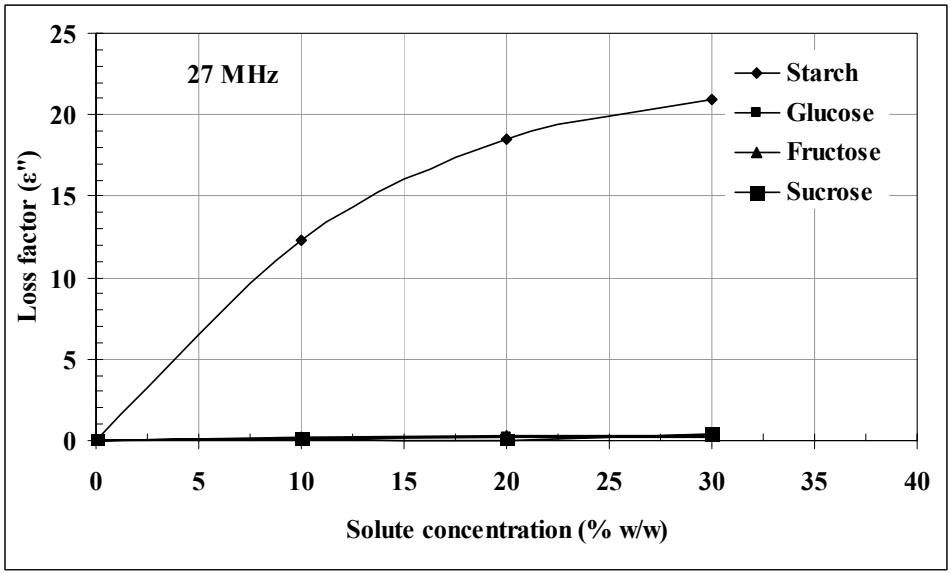

Figure 4.4.3.3. Dielectric loss (ε'') response to concentration variations at RF frequency (27.12 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

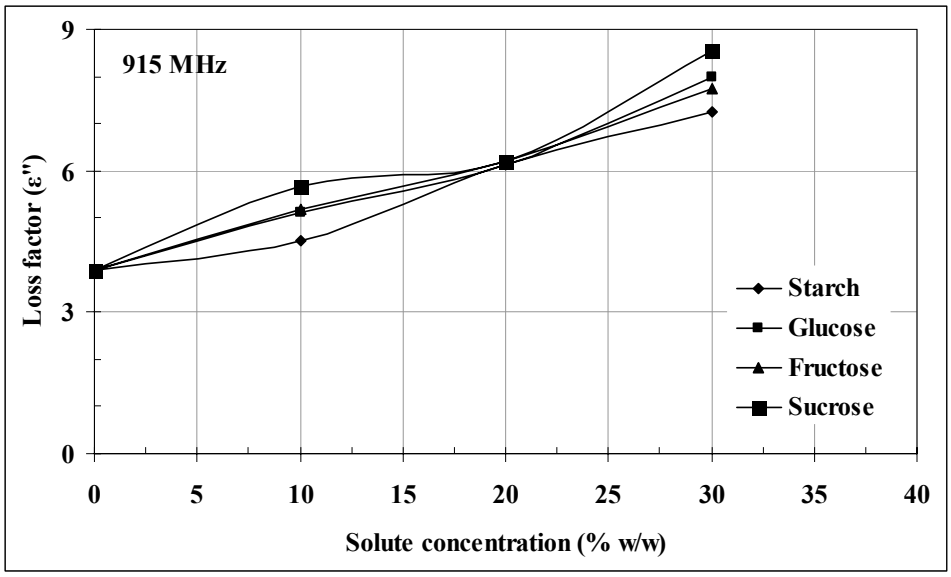

Figure 4.4.3.4. Dielectric loss (ε'') response to concentration variations at the MW frequency (915 MHz) for mono-, di-, and polysaccharide solutions of 20% (wt/wt).

4.5. CONCLUSION

MW and RF processing technologies present an attractive alternative to conventional retorting methods in commercial food processing, particularly when issues such as edge heating, cold spots, and run-away heating are successfully resolved. The dielectric properties of foods are one of the primary parameters responsible for the aforementioned issues, and are also critical for evaluating power attenuation and electric field intensity within treated materials. It is essential to accurately measure and quantify dielectric food properties for successful operation; studies need to extend to a product's constituents rather than bulk mixtures for better understanding of the interaction between particular foods and applied EM energy.

Because carbohydrates make up the major part of many foods, their individual contributions to the overall dielectric dispersion and absorption mechanism are important

for a comprehensive understanding of a food product's dielectric properties. Carbohydrates behavior in an EM field with variation in processing parameters such as temperature, frequency, and concentration were investigated to characterize the dielectric behavior of food products in general. For all carbohydrates used in this study, the ε' appeared to be fairly independent of field frequency from 10 MHz up to 1,000 MHz. Beyond the 1,000 MHz frequency, a significant and progressive decline was clearly observed. This behavior was interpreted in terms of the physicochemical properties of the solutions in which the viscous effect and formation and breaking of the water's H bond network were primary. The ε' also exhibited a gradual decrease with increasing medium temperature. This was attributed to the molecular thermodynamics model of dielectrics in which the resulting thermal agitation due to temperature increases always results in disorienting the dipoles and consequently decreasing the ε'. Furthermore, increasing carbohydrate concentrations resulted in depressing the ε' for all frequencies in the selected range of the spectrum, which was in agreement with the –H bonding sites concentration hypothesis.

Acknowledgements

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CHAPTER FIVE

DIELECTRIC DISPERSION OF FOOD PROTEINS: QUALITATIVE ANALYSIS

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5.1. ABSTRACT

Dielectric dispersion analysis was performed on aqueous solutions of Ovalbumin, Bovine Serum Albumin, β-Lactoglobulin, and Lysozyme at approximately 450 different frequencies between 5 MHz and 1.8 GHZ. Measurements were conducted using an open-ended coaxial probe at six concentrations and 25^{o}C. All examined proteins exhibited similar dielectric mechanisms for the selected concentrations and results agreed with previously published data. Increasing protein content resulted in continuous increments of the dielectric loss only at lower frequencies. Ionic release from proteins was evident from both the behavior of ε" and electrical conductivity. Previously reported δ-dispersions between β and γ-dispersions for protein solutions were observed, although at higher relaxation frequencies. Clearly separated δ-dispersions were observed at 550 MHz, 750 MHz, and 970 MHz, which we propose are a subset of a multiple dispersions that exist between the well-established β and γ-dispersions. We further hypothesize that

these already discovered and yet-to-be discovered dispersions are in some way responsible for the obscure behaviors, eruptions, successive boiling, and non-uniform heating commonly observed for liquid and semi-liquid biological materials when dielectrically heated in accordance with the well-documented phenomenon of migrating relaxation regions with product temperature.

5.2. INTRODUCTION

Use of electromagnetic (capacitive) energy (EME) in dielectric heating of biological materials at frequencies in the microwave (MW) and radio frequency (RF) bands of the spectra has rapidly increased over the past several decades. Numerous scientific and industrial fields have benefited from this technology since its discovery in the late 1700s by Michael Faraday (Swenson 1946). Currently EME is heavily used in a variety of fields, including chemical and biological sciences, medical and biomedical applications, and most recently, in the food processing industry. For example, EME can help extract chemical compounds (Gabriel et al. 1998), measure cell membrane thicknesses (Stuchly et al. 1982), produce heat (hyperthermia) to treat various diseases (Foster and Schwan 1989), kill insects in post-harvest agri-products, and pasteurize and sterilize food materials (Ryynanen 1995, Ikediala et al. 2000).

When a dielectric material is placed in an electromagnetic (EM) field, interactions between the material's constituents and the EM field are generally characterized by the material's dielectric properties, dielectric constant (ε') and loss factor (ε") (Mudgett et al. 1974). The ε', a measure of the electrical charges and molecular dipole dispersion, and ε", a measure of the electrical energy conversion into thermal energy within the material, are the primary parameters responsible for coupling EME to the dielectrically treated product (Mudgett 1985). They are the main parameters of Maxwell equations, which govern the distribution and transport of EME in dielectric heating systems. From an engineering viewpoint, dielectric parameters are the most important physical properties

associated with dielectric heating of materials (Mudgett 1986). Therefore, it is critical to have precise knowledge of their response to an applied EME in product and process development, and especially in the modern design of dielectric heating systems to meet desired process requirements. The need for such knowledge is even more apparent with the advance of computer modeling tools, which are increasingly used in the design and optimization of EME application systems and development of dielectric heating processes (Wig 2001, Pathak et al. 2003).

To simplify studying the dielectric properties of foods, product constituents have generally been divided into two main components: solids and water (Mudgett 1985). The major constituents making up the physical structure of biomaterials (carbohydrates, proteins, lipids, and salts) are commonly combined as the solid phase of the system, while water makes up the remaining part. Although much of this work is excellent, analysis and interpretations of the measured data based on this simplification has unfortunately failed to accurately explain the nature of the interactions between food materials and EM fields (Sun et al. 1995). Hence, dielectric investigation of biomaterials must be extended into studies of their major constituents and interactions with EM fields. The dielectric behavior of carbohydrates, proteins, lipids, and salts must be probed individually to gain a comprehensive understanding of the whole mixture. To begin this process, our group conducted dielectric studies on carbohydrates, for which results are reported separately. The current study is concerned with the dielectric behavior of common proteins of interest to dielectric heating of food products.

Early dielectric studies of protein solutions resulted in the discovery of three principal dispersions (α, β, γ) occurring respectively over the frequency ranges of approximately 0.01–10 MHz, 10 MHz–1 GHz, and 1–100 GHz (Kirkwood and Shumaker 1952, Dintzis et al. 1954, Fricke et al. 1956, Takashima and Schwan 1965, Grant et al. 1968, 1978, Pethig 1979). Pennock (1969) and Schwan (1965) appear to be the first to provide tangible interpretations and analysis of these dispersions. They explained that the first dispersion (α) was due to the relaxation of the protein molecule, the second dispersion (β) was due to the relaxation of water molecules bound to the protein, and the third dispersion (γ) was due to the relaxation of the bulk liquid surrounding the protein molecules (Pennock 1969, Schwan 1965). Considerable research has yielded new dispersion regions and new interpretations since these early efforts.

Thus far, the newly discovered dispersions fall between the β and γ dispersion regions (Essex et al. 1977). This region is of major importance to engineers and scientists involved in industrial applications of EM energy due to its inclusion of the industrial, scientific, and medical (ISM) frequencies (13.56 MHz, 27.12 MHz, 40.68 MHz, and 915 MHz) (Tang et al. 2001). The recently explored technology of industrially pasteurizing and sterilizing food products uses systems operating with frequencies centered at 27.12 MHz (RF) and 915 MHz (MW) (Wig 2001). Dielectric dispersions are typically accompanied by energy absorption and consequently, heat generation and dissipation. Thus, understanding of the primary mechanism responsible for these dispersions is not only necessary for molecule characterization, but utilizing them as a more efficient means of producing thermal energy and optimum systems design.

In this study, efforts are directed towards addressing issues pertaining to the behavior of proteins in solutions and how they affect the overall energy absorption and distribution within dielectrically heated food system. Emphasis is placed on understanding the underlying dielectric mechanisms at ISM frequencies, especially those related to dielectric heating of food materials. The primary objective of this investigation is to provide explanation as to how the protein constituents of a food product affect the overall energy conversion.

5.3. METHODS AND MATERIALS

The frequency-dependent dielectric response of protein solution samples at 25 ^{o}C was measured between 5 MHZ and 1.8 GHz using a system consisting of an Agilent (formerly Hewlett Packard) 4291B impedance analyzer with a calibration kit (Agilent Technologies, Palo Alto, CA), an open-ended coaxial probe, a custom-built test cell, and a VWR Model 1157 programmable circulator (VWR Science Products, West Chester, PA). The impedance analyzer was connected through an IEEE-488 (GPIB) bus to a desktop computer used with custom-designed software (DMS 85070, Innovative Measurements Solutions) to control the impedance analyzer and log the measured data. The electrical conductivity was measured using a Cole-Parmer Model 19950 bench-top conductivity meter (Cole-Parmer Instrument Co, Vernon Hills, IL).

Six purified proteins were selected for this investigation: 1) ovalbumin (A2412), 2) bovine serum albumin (BSA, A7030), 3) BSA (A7638), 4) lysozyme (L6876), 5) β-lactglobulin (BLG, L0130), and 6) β-lactglobulin (BLG, JE 001-3-922). The first five proteins were purchased from Sigma-Aldrich, St. Louis, MO, and the sixth from Davisco

Foods International, Le Sueur, MN. Selected proteins varied in molecular weight (Mw), structure, primary function, and isoelectric point (pI). Samples were prepared by adding appropriate amounts of proteins to obtain a total of six levels of concentrations (wt/wt) into a fixed amount of double de-ionized water with an average electric conductivity of 0.25 uS/cm. Each sample was prepared in a large beaker (300 ml), and then divided into three smaller beakers (50 ml) to obtain three measurement replicates taken 2 min apart. Samples were maintained at a constant temperature (≈ 25°C), continuously stirred, and securely covered to prevent evaporation for no longer than 4 min. Reported data points are averages of three replicates in which the calculated standard deviation was less than 5% for all measurements. Error bars and statistical analysis are omitted in this treatment for clarity of presentation.

Ovalbumin is a phosphorylated-glycoprotein from chicken egg white. The peptide portion of the molecule consists of 385 residues and has a Mw of 42.7 kDa. The carbohydrate and phosphate portions account for an additional 1,428 and 160 g/mol, respectively, giving a total Mw of 44.3 kDa. BSA A7030 and A7638 are single polypeptide chain proteins of about 583 amino acids and no carbohydrates; from 5–7 pH, they contain 17 intrachain bridges and one sulfhydryl group. The Mw of BSA was commonly cited as 66.1201 or 66.2672, but revised in 1990 to 66.430 kDa. A7030 is a globular protein with >98% purity, while A7638 is globulin-free with 0.99% purity. Lysozyme is a single polypeptide chain of about 129 amino acids cross-linked with four disulfide bridges and has a Mw of about 14.307 kDa. The protein content of lysozyme by UV absorbance is about 95%, with the reminder made up of buffer salts such as sodium acetate and sodium chloride. BLG L0130 contains A and B β-lactoglobulins with ~90%

(PAGE) purity and lyophilized powder with a total Mw of 36.6 kDa. BLG JE 001-3-922 is a native, undenatured 95% (98.3% dry basis) whey protein.

5.4. EXPERIMENTAL RESULTS

The dispersion curves obtained for all studied proteins at 20 mg protein/g water are shown in Fig. 5.4.1. The exhibited protein mechanisms were generally similar for the six levels of concentration and agreed fairly well with previously published results in the selected frequency band (5–1,800 MHz) (Oncley 1941, Harvey and Hoekestra 1972, Grant et al. 1978, Oleinikova et al. 2004). The dielectric dispersion, characterized by ε', decreased rapidly with increasing frequency in the low RF range (f <30 MHz), and appeared to approach a constant value in the high RF band (30 >f <300 MHz) and low MW band (300 >f <1,000 MHz), but began to decline at frequencies beyond 1,000 MHz. Although the decline of ε' is not clearly visible from Fig. 5.4.1 due to the limited upper frequency, tabulated data consistently demonstrated the mentioned decline (Table 5.4.1). This behavior conforms to the dielectric theory interpretations in which the sharp decline at low frequencies must be the last segment of the β-dispersion leg. Similarly, the sudden decline beyond the 1,000 MHz frequency marks the onset of the γ-dispersion region. Additionally, the effect of protein size is evident, in which the dielectric dispersion, and consequently the molecular relaxation time, is significantly depressed with increasing molecule size and geometry. Lysozyme, the smallest of all proteins with a Mw of 14.3 kDa, absorbed the highest energy due to its ability to reorient with the alternating EM field better than the much larger BSA molecules with a Mw of approximately 66.43 kDa.

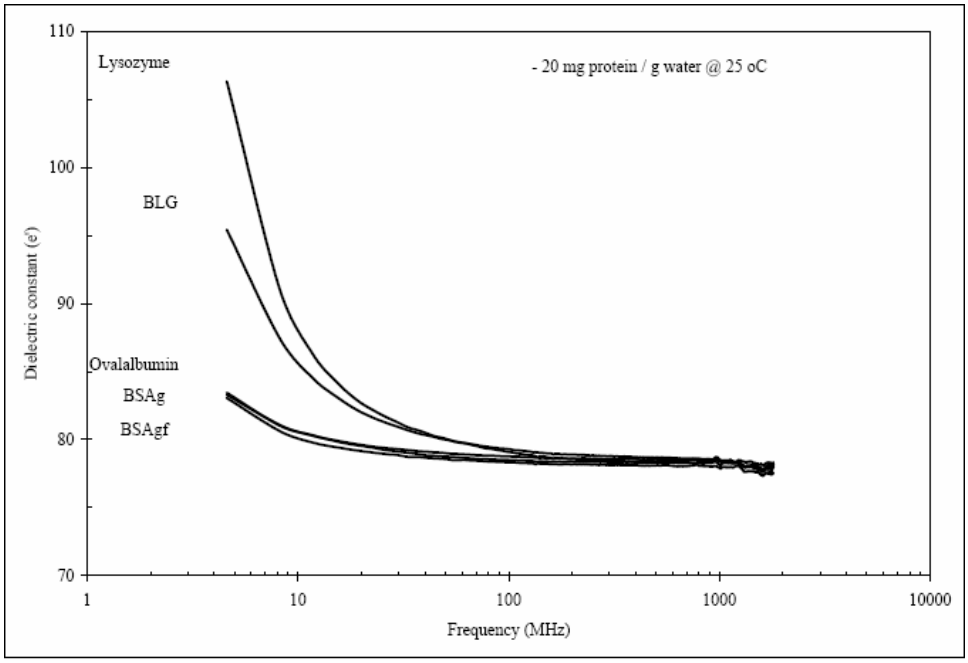

Figure 5.4.1. Dielectric constant (ε') (20 mg protein /g water) at 25 ^{o}C.

The dielectric loss factor (ε") demonstrated similar behavior for all examined samples, in that a sharp decline was evident in the low frequency range, minimal change in the intermediate range, and a minor yet progressive increase at higher frequencies (Figs. 5.4.2 and 5.4.3). This agrees well with previously published results (Oleinikova et al. 2004). It also confirms theoretical interpretations that the dielectric loss curve is a sum of bell-shaped dispersions that vary in their width and height based on the physical nature of the relaxing molecules in the continuum. Figure 5.4.2 shows that the segment of the curve from 5–100 MHz is clearly the last section of the β-dispersion region and the small segment beyond the 1,000 MHz sets the beginning for the γ-region.

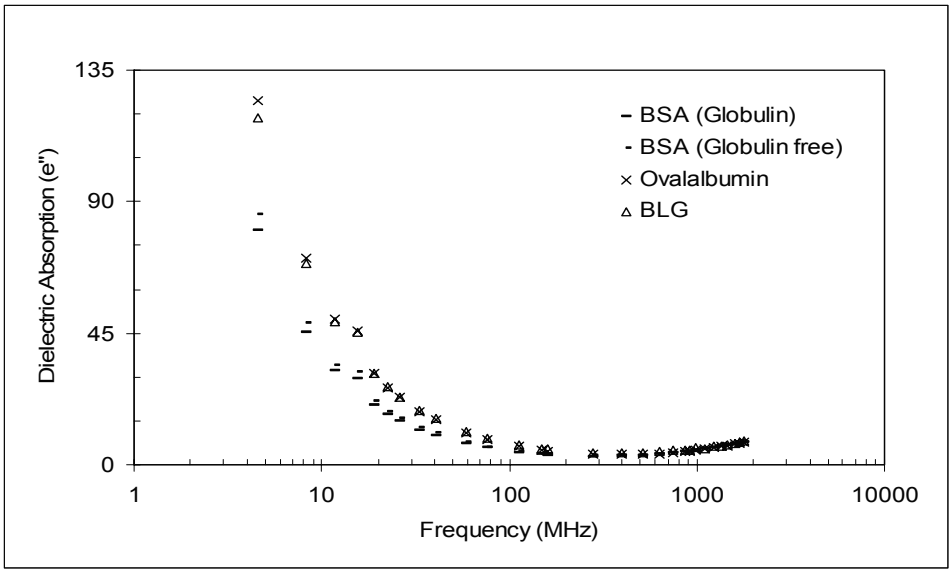

Figure 5.4.2. Dielectric loss of protein solutions at 20 mg protein/g water concentration and 25 ^{o}C.

Protein content influence on the dielectric behavior of mixtures is further amplified via the energy dissipation capability of media characterized by the dielectric loss factor, as depicted in Fig. 5.4.3. Increasing protein concentration continuously resulted in increments of the dielectric loss specifically at lower frequencies (RF band). In addition to the ε" contribution from the impurities introduced with the solutes, molecular rotation tumbling is anticipated to contribute significantly to the overall loss of the mixture. Therefore, the ε" is expected to increase with increasing protein content up to an optimum limit (not determined yet) where solute-solute interaction can no longer be ignored and decrements of ε" will eventually begin as a result of solute-solute binding and coagulation.

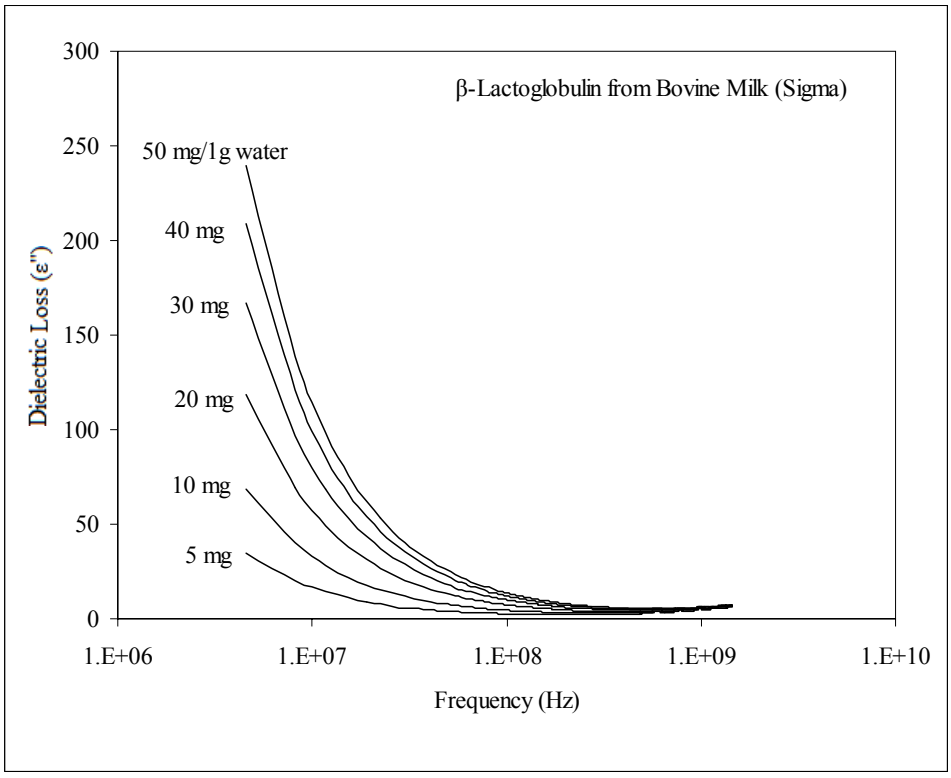

Figure 5.4.3. Dielectric absorption (loss) of non-enzymatic protein solutions.

Dielectric property and electrical conductivity data for selected frequencies (ISM) is presented in Table 5.4.1, which shows that for all proteins the electrical conductivity continuously increased with increasing concentration, quantitatively demonstrating the magnitude of ionic release from proteins and free ions introduced into the solution as impurities. The effect due to the amount of impurities that accompany the proteins is evident when comparing the values of μ for BLG obtained from Davisco Co. with those values for the high-purity protein obtained from Sigma-Aldrich Co. Similarly, increasing protein content caused an increase in the solution dielectric constant and loss factor, but only at low frequencies of the studied spectra. At higher frequencies, both ε' and ε" were significantly depressed. Figure 5.4.4 shows that the rate of increase at the lower

frequencies (slope) is appreciably greater than the rate of decrease at the higher frequencies for the same concentrations.

Table 5.4.1. Experimental data for the dielectric constant (ε), dielectric loss (ε"), and electrical conductivity (σ) of BLG, BSA, ovalbumin, and lysozyme protein solutions at selected ISM frequencies and protein contents at 25°C.

Beta-Lactglobulin (Davisco Co.) |		Frequency (MHz)											
		5		13		27		40		915		1800	
mg/g H_2O	σ (μS/cm)	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
0	0.37	78.01	0.00	78	0.01	78	0.09	78	0.16	78	3.61	77	6.97
5	129.00	83.62	47.93	80.80	18.33	80.01	9.11	79.81	6.36	79.56	4.13	79.06	7.71
10	244.67	87.16	76.44	82.23	35.06	80.48	17.30	80.06	12.08	79.82	4.61	78.24	7.49
20	476.00	95.43	177.22	84.03	67.28	81.17	33.19	80.34	22.93	78.53	5.00	78.15	8.13
30	639.00	100.38	240.38	85.67	90.78	82.07	44.79	80.97	31.02	78.39	5.74	77.80	8.59
40	829.00	104.49	311.05	85.81	117.23	81.27	57.77	79.91	39.95	76.65	5.92	76.10	8.08
50	975.00	107.01	359.16	86.70	135.38	81.60	66.61	80.08	45.96	76.19	6.50	75.52	8.63
Beta-Lactglobulin (Sigma-Aldrich Co.)													
0	0.37	78	0.00	78	0.01	78	0.09	78	0.16	78	3.61	77	6.97
5	94.50	83.17158	34.48035	80.35	13.17	79.86	6.56	79.74	4.71	80.19	4.35	79.45	7.63
10	174.30	85.12	68.66	79.55	26.21	78.35	13.03	78.03	9.15	77.90	4.39	77.15	7.44
20	311.00	92.27	118.82	82.59	45.30	80.47	22.51	79.87	15.73	79.05	4.92	78.16	7.94
30	446.00	96.73	167.10	83.60	63.48	80.71	31.47	79.90	21.91	78.33	5.29	77.44	8.17
40	515.00	100.27	208.69	84.09	79.14	80.54	39.12	79.56	27.11	77.45	5.53	76.61	8.26
50	584.00	102.52	239.16	84.09	90.65	80.02	44.76	78.89	30.99	76.50	5.72	75.67	8.17
Bovine Serum Albumin (Globulin-Free)													
0	0.39	78	0.00	78	0.01	78	0.09	78	0.16	78	3.61	77	6.97
5	68.80	81.23	24.61	80.20	9.16	79.97	4.59	79.93	3.26	79.66	4.04	79.31	7.52
10	123.20	82.14	46.36	80.33	17.17	79.88	8.47	79.78	5.92	79.39	4.23	78.91	7.55
20	237.00	83.28	85.48	80.15	31.50	79.36	15.45	79.12	10.70	78.46	4.46	77.96	7.63
30	331.00	84.66	121.44	80.18	44.69	79.11	21.86	78.78	15.07	77.81	4.71	77.39	7.73
40	412.50	85.61	152.46	79.91	56.05	78.63	27.35	78.23	18.82	77.04	4.91	76.63	7.83
50	494.00	86.30	180.80	79.41	66.37	77.93	32.30	77.50	22.19	76.09	5.02	75.67	7.73
Bovine Serum Albumin (Globular)													
0	0.21	78	0.00	77.95	0.01	77.94	0.09	77.94	0.16	77.88	3.61	77.26	6.97
5	65.70	79.92	22.85	78.92	8.48	78.74	4.22	78.69	2.97	78.68	4.01	78.31	7.47
10	119.10	81.34	42.73	79.53	15.86	79.10	7.81	78.97	5.45	78.76	4.22	78.29	7.65
20	221.00	83.06	80.02	79.66	29.55	78.92	14.50	78.67	10.03	78.05	4.54	77.49	7.85
30	314.00	84.06	114.50	79.24	42.14	78.20	20.62	77.86	14.22	76.97	4.78	76.44	7.92
40	400.00	85.50	145.92	79.32	53.73	78.01	26.25	77.58	18.09	76.31	5.03	75.74	8.07
50	477.00	85.13	173.12	77.93	63.65	76.39	31.07	75.90	21.39	74.38	5.16	73.73	7.96
Ovalalbumen													
0	0.24	78	0.00	78	0.01	78	0.09	78	0.16	78	3.61	77	6.97
6	105.80	82.68	40.96	81.11	15.54	80.51	7.83	80.29	5.53	80.17	4.25	80.09	7.83
7	122.20	82.68	47.80	81.05	18.05	80.43	9.04	80.20	6.33	80.00	4.32	79.87	7.80
8	145.70	82.47	56.27	80.69	21.13	80.01	10.55	79.77	7.37	79.59	4.29	79.34	7.81
10	179.80	82.93	69.33	80.91	25.87	80.16	12.84	79.91	8.91	79.67	4.29	79.55	7.63
13	231.00	83.05	88.42	80.63	32.78	79.82	16.11	79.53	11.09	79.06	4.41	79.01	7.73
20	349.00	83.44	124.41	80.16	45.83	79.20	22.37	78.86	15.39	78.28	4.52	78.11	7.71
Lysozyme													
0	0.21	78	0.00	78	0.01	78	0.09	78	0.16	78	3.61	77	6.97
5	424.00	87.82	150.40	81.58	55.27	80.36	26.85	80.01	18.41	79.54	4.85	79.11	8.18
10	724.00	95.12	281.97	83.36	103.43	80.98	50.02	80.32	34.10	79.03	5.59	78.61	8.47
20	1366.00	106.32	480.85	85.58	176.13	81.57	85.16	80.52	58.06	78.42	6.83	77.93	9.06
30	1834.00	117.72	675.48	87.43	246.56	81.95	119.02	80.55	81.03	77.66	7.96	77.13	9.63
40	2260.00	128.74	850.35	89.02	309.30	82.20	149.15	80.50	101.44	76.91	8.96	76.35	10.15
50	2690.00	131.15	945.50	85.64	343.46	77.93	165.70	76.03	112.72	72.42	9.27	71.80	9.97

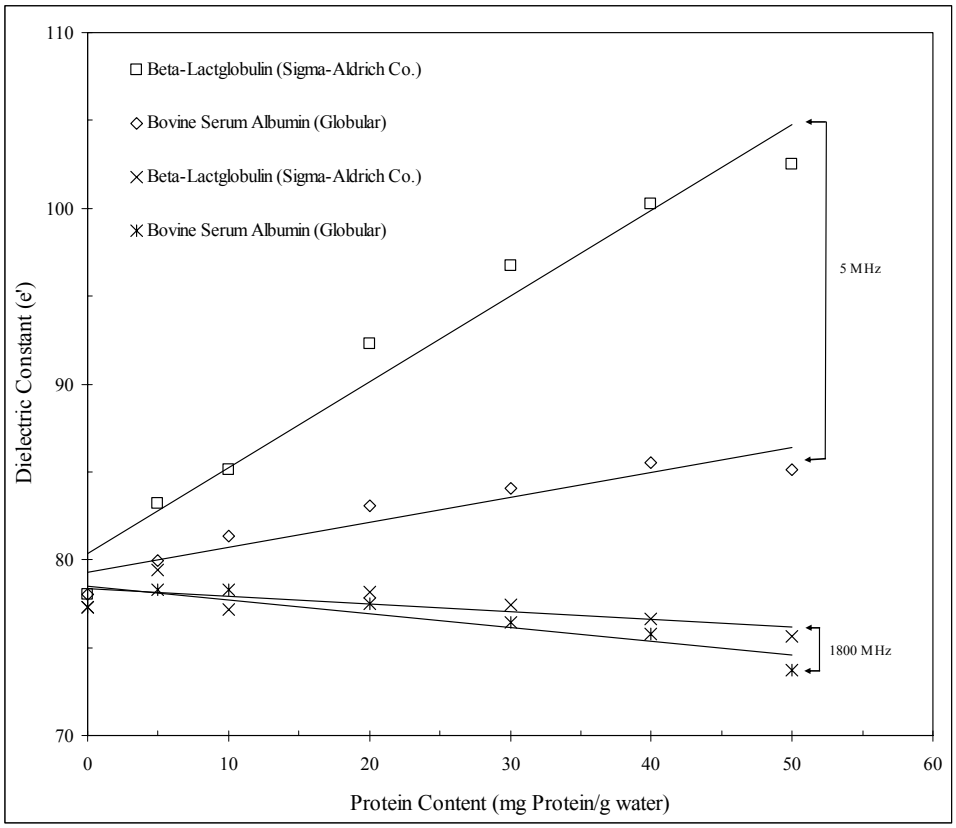

Figure 5.4.4. Dielectric loss response to variation in protein content in an aqueous solution (mg protein/1 g water) at 25^{o}C as a function of frequency in the RF and MW bands of the EM spectrum.

The dielectric behavior of lysozyme, although similar to other proteins, exhibited a larger magnitude of change in both its absorption and loss mechanisms (Table 5.4.1). This behavior was further confirmed by examining the electrical conductivity of the solutions, where lysozyme clearly demonstrated a significant increase over other proteins (Figs. 5.4.2 and 5.4.3). A linear relationship ($\sigma_{Lys} = 50.0*C_{Lys} + 252$; $R^2 = 0.9922$) was obtained for the electrical conductivity (σ_{Lys}) as a function of protein content (C_{Lys}) for all solutions, with lysozyme having the largest slope (Fig. 5.4.5).

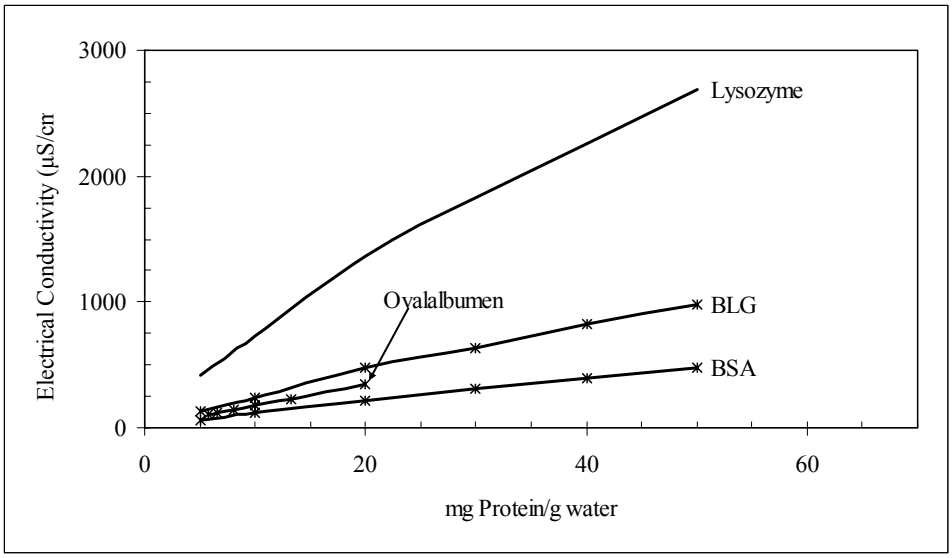

Figure 5.4.5. Measured electrical conductivity (σ) of protein solutions (20 mg protein/ml) at 20°C.

Experiments conducted by Grant (1966) and Moser et al. (1966) on BSA revealed an additional δ-dispersion region between the well-known β and γ-dispersions. A later study by Essex et al. reported in 1977 an additional two δ-dispersions, bringing the total dispersions in a protein solution to a clearly separated six (α, β, δ_1, δ_2, δ_3, and γ). Although the three new dispersions were not clearly observed for BSA solutions in this study at the reported critical frequencies (15 MHz, 100 MHz, and 250 MHz), they nevertheless surfaced for BLG solutions at much higher frequencies (550 MHz, 750 MHz, and 970 MHz) (Figs. 5.4.6 and 5.4.7).

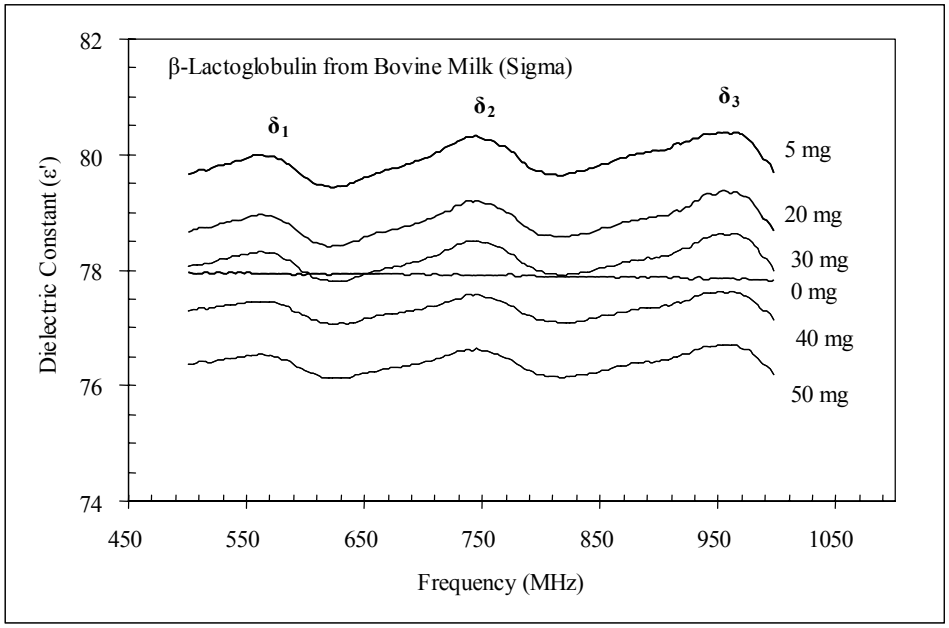

Figure 5.4.6. Dielectric dispersion of BLG solutions with three observed (δ) dispersions for five levels of concentrations at room temperature (25^{o}C).

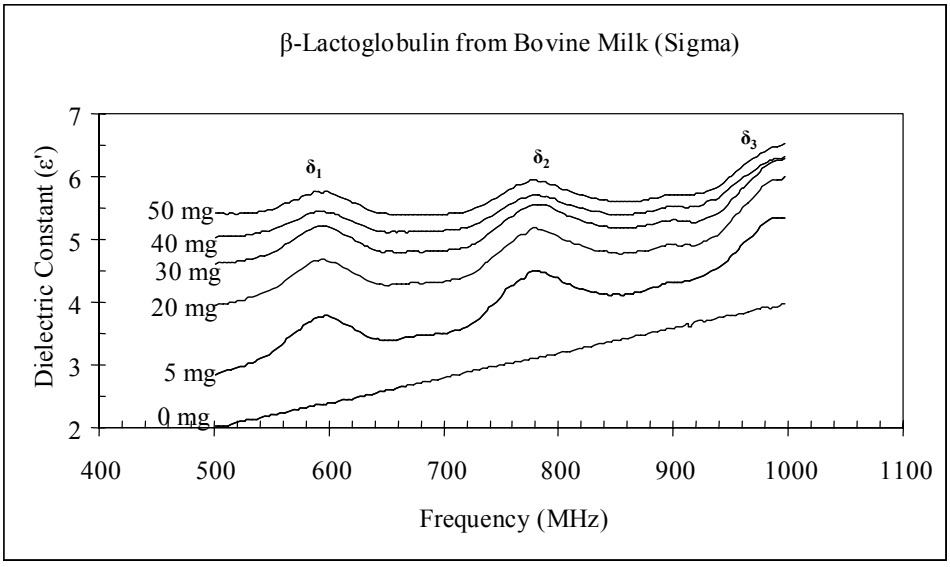

Figure 5.4.7. Dielectric absorption of BLG solutions with three observed (δ) dispersions for five levels of concentrations at room temperature (25°C).

5.5. ANALYSIS AND DISCUSSION

According to the general theory of dielectrics, if a pure substance has only one type of polar molecule, the dielectric dispersion curve is expected to fall from one plateau to another as the field frequency is increased. When a mixture includes two polar substances, two dispersions are expected. Hence, if one solute (polar) such as a protein is dissolved in water, one dispersion due to the relaxation of the solute molecules will occur, and another due to the relaxation of the polar solvent molecules.

Experimental work conducted between the 1920s and 1970s resulted in the discovery of three dispersions (α, β, and γ), and in recent years (including the current study), three more dispersions (δ_1, δ_2, and δ_3) were added to the total observed dispersions of biological molecules in water (Figs. 5.5.1 and 5.5.2) (Grant et al. 1968, Essex et al. 1977, Oleinikova et al. 2004). Although researchers agree on the presence of these dispersions in the investigated frequency bands, their interpretations and sources differ.

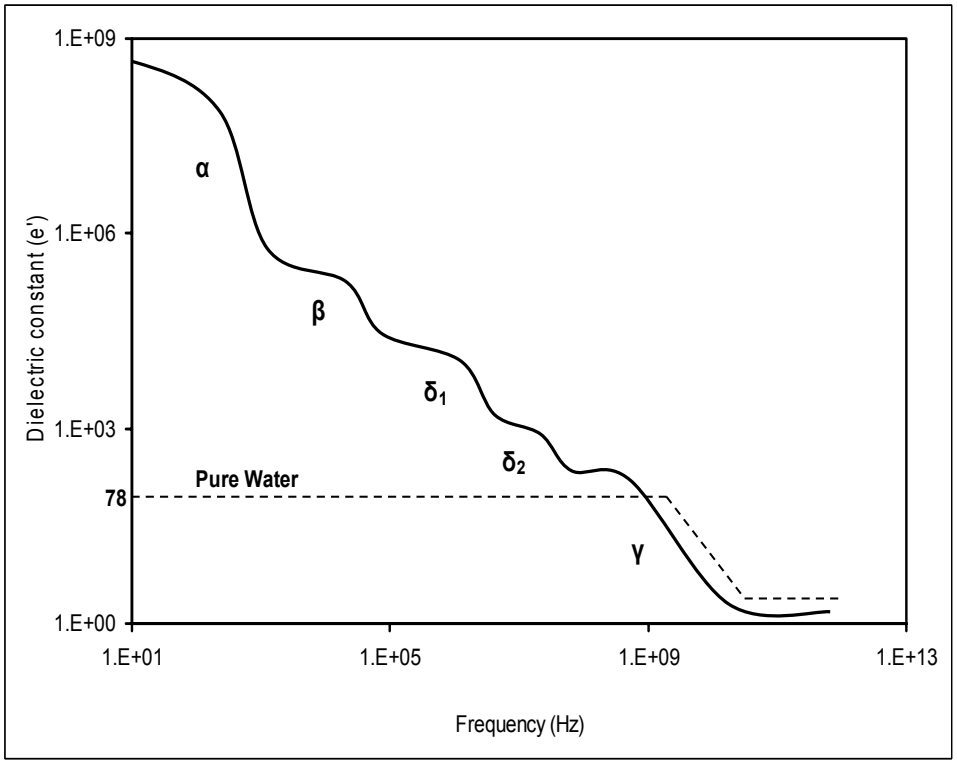

Figure 5.5.1. Typical dielectric behavior of protein solutions.

To begin, the γ-dispersion has been extensively investigated and well-characterized and there is nothing to add as a result of this work. Debye (1929) and Hasted (1973) determined its origin was due to the rotation of free water molecules with a relaxation frequency around 20 GHz at 25^{o}C.

The α-dispersion, the least understood as of today, is generally attributed to either relaxation of counterions surrounding the charged biomolecules (Foster and Schwan 1989) or migration of ions through voids in membranous materials (Grant et al. 1978). For nonstructural biological materials (tissues and organelles) dissolved in a continuous phase such as water, the first interpretation is the most likely mechanism. This is supported by the physical mechanism underlying the behavior, in which at low

frequencies the ionic conduction contribution to the overall energy absorption by the system far exceeds the contribution of all other mechanisms. Mudgett et al. (1974) and Guan et al. (2002) established that the total dielectric absorption (ε''_t) of a system at any frequency is a two-component quantity: absorption due to dipole polarization (ε''_d) and absorption due to ionic conduction (ε_σ) (i.e., $\varepsilon''_t = \varepsilon''_d + \varepsilon''_\sigma$).

The loss contribution due to ionic conduction is inversely proportional to frequency, causing its effect on the overall absorption to diminish as frequency is increased:

$$\varepsilon_\sigma'' = \frac{\sigma}{2\pi f \varepsilon_0} \tag{5.5.1}$$

where σ is the electrical conductivity (S/m), ε_o the free space permittivity (8.854×10^{-12} F/m), and f the EM wave frequency (Hz). The presence of large quantities of charge carriers (e.g., salts and electrolytes) in the system, as in the case of a lysozyme solution with a high concentration of salt residues from the purification process, further enhances this ionic effect according to Eq. 5.5.1 (Figs. 5.4.2, 5.4.3, and 5.4.5).

The β-dispersion region is usually interpreted in terms of two primary mechanisms: 1) dispersion due to Maxwell-Wagner effects (Grant et al. 1986), and 2) dispersion due to partial (Pennock 1969) or complete relaxation of larger solute molecules (Oncley 1938). Although the mechanism due to Maxwell-Wagner effects, which results from charge accumulation at the various boundaries separating a mixture's constituents, can have considerable contribution to the β-dispersion, it is most likely due to the partial reorientation of the solute molecules (Gabler 1978). This is because for

binary mixtures, the boundary effect is minimal compared to the influence of varying solute molecular orientations based on size and geometry. At low frequencies large molecules (proteins) in water have sufficient time to reorient themselves in an alternating EM field where the retarding frictional forces acting on them are small compared to the electrical orienting forces. As the field frequency is increased, the frictional forces are no longer negligible, and the large molecules cannot completely reorient and equilibrate. Here frictional forces retarding the biomolecular orientation completely overwhelm the electrical orienting forces, so the permanent dipoles of the biomolecules make no contribution to the dielectric constant.

Instead of analyzing the recently discovered δ-dispersions separately as has been the case in previously published studies, we propose to include them as subunits of the β-dispersion and further argue that the β-dispersion is a summation of a very large number of δ-dispersions for complex mixtures such as foods.

$$\beta - dispersion = \sum_{i=1}^{n} \delta_i \tag{5.5.2}$$

This hypothesis can be instinctively extended to the other dispersion regions (α and γ) and theoretically deduced from the argument made for the β-dispersion. We believe that as measurement techniques and devices advance over the coming years, experimental data will eventually emerge to validate this hypothesis. For now, discussion will be limited to the β-dispersion region, for which we have experimental data to support. Since the δ-dispersion was first mentioned in the late 1960s (Grant 1966, Pethig 1979), two more dispersions were added a few years later (Essex et al. 1977), bringing

the total number of dispersions to three in the 1–1,000 MHz range. This trend, although weak, seems to keep progressing with advances in measurement devices and techniques. Intuition is further supported by the possible physical interpretation of observed consecutive and intermittent boiling and eruptions in dielectric heating of liquids and semi-solid materials. This can safely be attributed to the multiple molecular relaxations of constituents comprising dielectric mixtures in the same manner as when pure water boils once its molecules have dispersed and molecular rotation ensues.

Proton fluctuation, side chain rotation, bound water relaxation, and local atomic and electronic polarization mechanisms have also been proposed to account for δ-dispersion(s), with each arguing that only one mechanism is most probable over the others. Although justified in previous years before additional dispersions were discovered, the debate must now be resolved by attributing each mechanism to a corresponding δ-dispersion; summing them up will provide satisfactory interpretation of the overall β-dispersion. Currently, only quantitative characterization is possible for the dispersion due to local atomic and electronic polarization. Detailed theoretical and quantitative analyses of this mechanism were performed in this study, with results reported in a separate chapter.

Kirkwood and Shumaker (1952) initially proposed a proton fluctuation mechanism to account for dispersions between the β and γ regions. Their underlying hypothesis was that the polarization of a biomolecule was most likely due to the fluctuation of the mobile protons along the basic sites of the molecule in the direction of the electric field. Takashima (1972) further investigated this assumption, and found

supporting experimental results that agreed fairly well with the theoretical ones derived by Kirkwood and Shumaker (1952). Moser et al. (1966) showed that the relaxation frequency values of 33 MHz and 160 MHz were appropriate for BSA solutions near the isoelectric point based on the assumed mobile proton fluctuations. South and Grant (1974) also considered the phenomenon of proton fluctuation and concluded that a δ-dispersion is possible if the macromolecule rotational correlation time is much greater than the proton fluctuation time.

Pennock and Schwan (1969) proposed a polar side-chain relaxation mechanism as the underlying cause for the δ-dispersion they observed for a hemoglobin solution. They conducted measurements of permittivity and conductivity at five concentrations over the frequency range 1–1,200 MHz and concluded that dispersions below 100 MHz were most likely due to relaxation of protein side-chains. Essex et al. (1977) provided a similar interpretation for BSA solutions due to corresponding findings.

The relaxation of water that is tightly bound to biological molecules is another proposed mechanism by various authors as the cause for observed δ-dispersion(s) (Harvey and Hoekestra 1972, Schutz and Warshel 2001, Suherman et al. 2002, El Moznine et al. 2003). The underlying hypothesis for this mechanism is that water molecules are unable to rotate in an alternating EM field at frequencies below 1 GHz and therefore contribute to the permittivity of the solution only through their atomic and electronic polarization. Schwan (1983) and Grant et al. (1978, 1968, 1986) proposed that the δ-dispersion was most likely due to the relaxation of bound water present in hemoglobin, egg albumen, BSA, and myoglobin, respectively. Schwan (1965) showed

that the permittivity data are consistent with a hydration of 0.3 g bound water per gram of protein. As for BSA, Grant (1966) obtained a hydration of 0.2 g bound water per gram of protein.

Regardless of the accuracy of assigning mechanisms to the observed dispersions between the β and γ dispersions, the accumulative overall effect of their presence on the material to be dielectrically heated is the primary factor in dielectric heating. If one single solute (biomolecule) experiences multiple dispersions with variations in frequency, a multitude of biomolecules in a biological mixture (food materials) will eventually result in a very large number of dispersions, each accompanied with significant thermal energy release. Operating MW and RF ovens at fixed frequency does not necessarily constitute one relaxation region as long as the products being radiated accumulate thermal energy and their temperatures keep increasing. Constant temperature increase consequently causes the dispersion regions to migrate to higher relaxation frequencies, as indicated in Fig. 5.5.2. Figure 5.5.2 also demonstrates that as long as a product made up of a very large number of constituents is constantly radiated with EM energy, its temperature will continue to increase, causing the critical frequency of each constituent to shift to a higher one. When the design temperature is reached (e.g., 121^{o}C for food sterilization), it is expected that the majority of the constituents have reached their critical relaxation frequencies and significantly contributed to the overall thermal energy generated within the product.

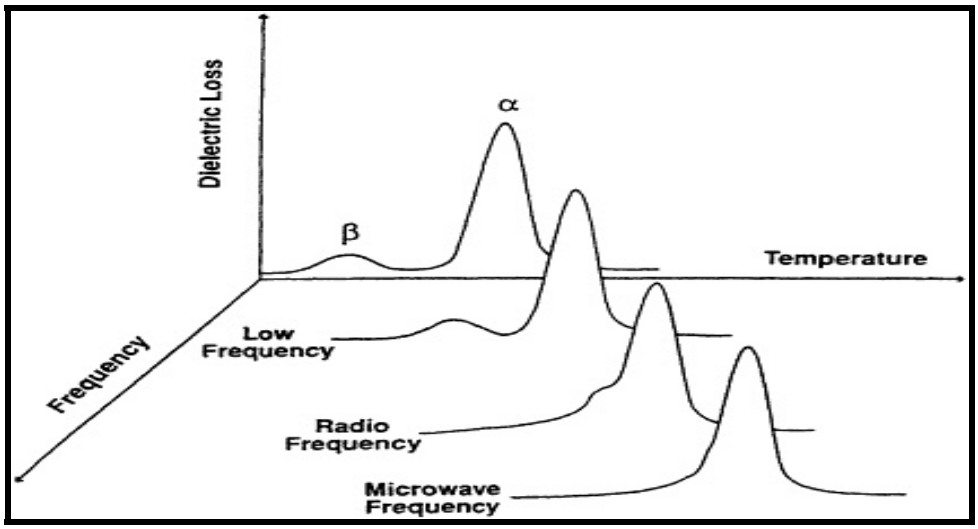

Figure 5.5.2. Electromagnetic dispersion region migration with both increasing temperature and frequency (National Research Council et al. 1994).

5.6. SUMMARY AND CONCLUSIONS

Although use of MW ovens for domestic food processing has enjoyed substantial growth over the past few decades, similar growth in commercial and industrial use is yet to be realized. This is primarily due to many unanswered questions from the public and regulatory organizations about equipment utilizing EM radiation as the source of energy for industrial food processing, medical procedures, and other applications involving biological materials. For food processors, answers must be provided to whether the cold spots in processed products can be eliminated or at least accurately and consistently located for any product under any processing conditions. Answers must also be provided to whether a treatment process can be established where the parameters involved, including input power, processing time, heating rate, and process deviations, can be successfully monitored and controlled.

The following conclusions may be drawn from this study:

1. All examined proteins exhibited similar dielectric mechanisms for the selected concentration levels and results agreed with previously published studies.
2. The α and γ-dispersions were clearly observed for all proteins for which the last α-dispersion curve segment was evident in the interval 5–10 MHz of the spectrum and the initial stage of the γ-dispersion was observed at frequencies beyond 1 GHz.
3. Increasing protein size caused a significant depression in the solution's dielectric constant and loss factor.
4. Increasing protein content resulted in a continuous increase in the dielectric loss and thermal energy dissipation at low frequencies. However, continual increase of the ε" at lower frequencies is expected to subside at maximum concentration levels due to increasing molecular interactions and binding. The influence of protein content also resulted in a gradual increase of ε' at low frequencies and gradual decrease at higher frequencies. This behavior must be taken into account when designing equipment and processes that for EME applications at higher frequencies (Mw) to biological materials need only consider the effect of the solvent molecules, primarily water in food processing.
5. Ionic release from proteins was evident from both the behavior of ε" and electrical conductivity. Both parameters continuously increased with increasing protein content. Although ionic release was observed that confirmed previously reported observations, caution must be taken when trying to quantify their contribution to the overall dielectric mechanism, for their effect is still highly influenced and remains to some degree masked by the ionic contribution from introduced impurities with the samples.

6. Sub-dispersions (δs) between β and γ-dispersions for protein solutions were observed, albeit at higher relaxation frequencies than those reported in prior investigations. Clearly separated delta dispersions were observed at frequencies of 550 MHz, 750 MHz, and 970 MHz. We propose that these delta-dispersions are a sub-unit of multiple dispersions between the β and γ-dispersions. We anticipate that as measurement devices and techniques advance over the coming years, additional dispersions are expected to surface. We hypothesize that these already discovered and yet-to-be discovered dispersions are in some way responsible for the eruptions, successive boiling, and non-uniform heating commonly observed for liquid and semi-liquid biological materials when dielectrically heated in accordance with the well-documented phenomenon of migrating relaxation regions with product temperature.

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CHAPTER SIX

DIELECTRIC DISPERSION OF FOOD PROTEIN SOLUTIONS: QUANTITATIVE ANALYSIS

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6.1. ABSTRACT

Contribution of individual proteins to the dielectric loss and consequent thermal generation of dielectrically heated biological materials was experimentally investigated and found to have greater effect at low frequencies, especially at the newly explored radio frequency (RF, 27 MHz) for industrial pasteurization and sterilization of food products. In this study, dielectric dispersion analysis was performed on aqueous solutions of ovalbumin, bovine serum albumin (BSA), β-lactoglobulin (BLG), and lysozyme at approximately 450 different frequencies between 5 MHz and 1.8 GHZ. Measurements were conducted using an open-ended coaxial probe at six concentrations and 25^{o}C. All proteins exhibited similar dielectric properties at all examined concentrations. Theoretical calculation of the local dielectric constant (ε') of individual proteins resulted in an average value of 2.7, which agreed with previously reported data. A derived mixture equation provided results that agreed with experimental data at frequencies close to 915 MHz. An increase in the physical size of a protein resulted in a decrease in the overall

electromagnetic absorption of the mixture. Similar effect was observed as protein concentration increased, with more pronounced effects on the dielectric increments (Δε') and absorption decrements (Δε")

6.2. INTRODUCTION

The use of dielectric heat on biological materials has slowly increased over the past few years, but the technology is yet to be optimally utilized. The most notable use of dielectric heating is on foods in ovens operating at microwave (MW, 815 and 2,450 MHz) and radio frequency (RF, 27 MHz) ranges of the electromagnetic (EM) spectrum (Zhao et al. 2000). The greatest application of MW technology is consumer and food service heating, thawing, and cooking foods on a commercial scale. However, use of MW heating to sterilize food is still plagued by several issues and very few systems are in use commercially (Tops 2000). Problems include cold spots at non-predictable locations, edge heating, runaway heating, sudden bursting of package seals (solid and semi-solid products), product rupture, and recursive boiling (liquids). These anomalies appear to stem from a lack of understanding of the underlying mechanism of the interactions between the material and applied EM energy. Development of the few commercially available systems was unfortunately accomplished via mainly trial and error rather than a systematic, theoretically driven approach based on well-defined engineering rules and principles. Hence, researchers of dielectric heating reach inconsistent and even conflicting conclusions about the effectiveness and advantages of dielectrically processing biological materials relative to conventional heating methods.

Unlike conventional heating in which EM radiation (heat) is transferred from the surface of the product to the interior, dielectric heating is volumetric in nature, which means that the heat is generated throughout the bulk of the material (Wig 2001). This stems from the interaction of radiation in the dielectric frequency range, which causes heat to be generated via molecular rotation and translation within the volume of the material. Since the phenomenon is molecular in nature, the generated heat is necessarily uniform throughout, provided the material consistently has the same characteristics at the molecular level and the electric field strength (local) is uniform. If either of these factors change, the amount of heat generation and transport within the material will vary. This variation is due to molecular non-uniformity, and is generally described quantitatively by two numbers: the dielectric constant ε' and loss factor ε". These two quantities, or dielectric properties, are the primary parameters controlling the amount of EM stored and dissipated within materials that are dielectrically heated (Mudgett 1985, Von Hippel 1995; Tang et al. 2001). The rate of heat generation per unit volume P_{av} at a particular location in a food during MW and RF heating is given by the equation (Feng 1998):

$$P_{avg} = 2\pi\varepsilon_o\varepsilon'' f E^2 \tag{6.2.1}$$

where f is the frequency (Hz) and E is the electric field intensity (V/m).

According to this formula, the amount of heat generated at any location within a food product for a selected frequency is governed chiefly by two parameters: ε" and E. E is a process parameter that can be numerically quantified at any location via solving the wave equations with the appropriate boundary conditions (Metaxas and Meredith 1983); its magnitude can be indirectly manipulated via the input power. The ε", on the other

hand, is a constitutive property of the material that characterizes the energy dissipation as a result of the EM-material interactions at the molecular level. Therefore, if one is capable of quantifying and controlling the magnitude of ε", non-uniformity and runaway heating can be easily controlled or significantly minimized. Accurate quantification and prediction of ε" is essential for both quantifying the heat generation per unit of time and the electric field distribution within the material. It is then obvious that the detrimental issues associated with dielectric heating of biological materials relate to the ε" more than the E, which has been the focus of the majority of the research for the past several years. Efforts must therefore shift towards understanding, characterizing, quantifying, and predicting ε" before uniform heating can be attained.

Minimal research has exclusively focused on understanding the underlying mechanisms contributing to the dielectric properties (ε' and ε") of biological materials. Studies of the dielectric properties of complex biological systems such as foods are generally conducted by modeling the system with two main components: solids and water (Mudgett et al. 1977). The major macromolecular constituents of the system—carbohydrates, proteins, lipids, and salts—were historically grouped together as the solid phase of the system, with water making up the remaining part. Although much of this work is excellent, analysis and interpretation of the measured data based on this simplification has unfortunately failed to accurately explain the nature of the interactions between complex biological materials and an EM field (Sun et al. 1995). Furthermore, results from theoretically derived models based on this simplification fail to predict how materials behave when treated with EM under different processing conditions. It has also, until fairly recently, been difficult to replicate experimental data under different physical

and processing conditions (Mudgett et al. 1974), suggesting that dielectric investigations of food materials be extended to the major constituents of foods, composites of these constituents, and their interactions in an EM field. The dielectric behavior of carbohydrates, proteins, lipids, and salts must be evaluated individually and in combination to gain an accurate understanding of how foods will behave in dielectric heating systems. The current study involves the dielectric behavior of common food proteins in an aqueous medium at RF and MW frequencies used in food processing applications.

Efforts in this study are directed towards addressing certain issues pertaining to the behavior of proteins in solutions and how these properties affect the overall energy absorption and distribution within food to be dielectrically heated. Emphasis is placed on understanding the underlying dielectric mechanisms at the Industrial, Scientific, and Medical (ISM) frequencies, especially those related to industrial dielectric heating of food materials (27.12 and 915 MHz). Among the objectives of this investigation is to provide an explanation of how protein constituents of food products affect the overall energy conversion and contribute to overall dielectric properties of a food.

6.3. METHODS AND MATERIALS

6.3.1. Protein Molecule Dielectric Dispersion

Although extensive dielectric studies on proteins date back to the early 1930s, none of them have investigated the mechanism of EM absorption and the consequences of thermal generation and dissipation. Conversely, most of the previously conducted

research was directed towards either developing accurate techniques for measuring the properties of biological dielectrics (Fricke et al. 1956, Von Hippel 1995) or physical and chemical characterization of biomolecules in a relatively pure state (Grant et al. 1978, Foster and Schwan 1989, Oncley 2003, Oleinikova et al. 2004).

Among the earliest studies of the dielectric behavior of protein solutions are those of Wyman and Oncley in the early 1930s (Wyman and McMeekin 1933, Oncley 1938). They are believed to be the first to undertake large-scale dielectric studies of biomolecules, individual amino acids, and large protein molecules in solutions. Oncley (1941) measured the dielectric dispersion in 13 protein solutions and deduced the dipole moments and molecular shapes. He observed a dispersion in the frequency band centered around 2 MHz that he attributed to protein relaxation. Buchanan et al. (1952) conducted measurements above the 3 GHz band and concluded that dispersion(s) exist between the 2 MHz (Oncley highest frequency) and 3 GHz frequency bands (Haggis et al. 1951, Buchanan et al. 1952).

When biological mixtures are simplified into water and solids, dielectric analysis can be directed towards characterizing the behavior of solids and their interactions with water molecules. This simplification is necessary because of the ambiguous and complex nature of the bounding mechanism of water molecules to macromolecules such as proteins. Due to the pioneering work of Debye (1929) and Onsager (1936) and numerous descriptions of the dielectric properties of pure water in research articles and books (Hasted 1973), such predictions are now simple. Efforts should therefore be directed towards investigating the dielectric behavior of the solute molecules (proteins) and their

interactions in pure liquid water. Hence, if an aqueous protein solution is comprised of only protein molecules (a) and water (b) occupying a total volume of (V) and their volumes assumed to be additive, then

$$V = v_a V + v_b V \tag{6.3.1.1}$$

where v_a and v_b are volume fractions of components *a* and *b*.

For linear dielectrics (e.g., E and D are independent of ε), the constitutive law states that the average electric displacement (D_{avg}) is directly proportional to the applied average electric field (E_{avg}) and the proportionality parameter is the material's average permittivity (ε_m). According to Sadiku (2000), this is written as

$$\varepsilon_m = \frac{D_{avg}}{E_{avg}} \tag{6.3.1.2}$$

But, by definition,

$$D_{avg} = \frac{1}{V}\int_V DdV = \frac{1}{V}\left[\int_{Va} DdV_a + \int_{Vb} DdV_b\right] = v_a D_{a_{avg}} + v_b D_{b_{avg}} \tag{6.3.1.3}$$

Similarly,

$$E_{avg} = v_a E_a + v_b E_b \tag{6.3.1.4}$$

Substituting Eqs. 6.3.1.3 and 6.3.1.4 into Eq. 6.3.1.2 and simplifying yields

$$\varepsilon_m = f_a v_a \varepsilon_a + f_b v_b \varepsilon_b \tag{6.3.1.5}$$

$$1 = f_a v_a + f_b v_b \tag{6.3.1.6}$$

where $f_a = \frac{E_{a\,avg}}{E_{avg}}$ and $f_b = \frac{E_{b\,avg}}{E_{avg}}$. Rearranging Eq. 6.3.1.5 yields

$$\varepsilon_m = \varepsilon_b + (\varepsilon_a - \varepsilon_b) v_a f_a \text{ or } \varepsilon_m = \varepsilon_b + (\varepsilon_a - \varepsilon_b) v_a f_a \tag{6.3.1.7}$$

Equation 6.3.1.7 offers a simple tool to account for the contribution made by the protein molecules to the overall solution permittivity, except for the task of finding the field fraction f_a (or f_b if needed). Although exact values for these parameters have been obtained for limited cases such as parallel slab apparatus and infinitely diluted dispersions (Reynolds and Hough 1957), approximate calculations must be performed for all other cases (e.g., the electric field within the suspended particle to quantify f_a or f_b).

The average value of the field within a particle depends chiefly upon its geometry, dielectric constant, and the average field and dielectric constant of the bulk liquid surrounding it. If a particle is assumed to be suspended in a homogenous medium with a dielectric constant ε_s, then the most common approximation is to make $\varepsilon_s = \varepsilon_b$ (i.e., making the dielectric constant of the surroundings equal to that of the pure solvent) (Hagmann et al. 1992). The geometry of the molecule is assumed to be spheroid, for which the induced field within its molecules can then be approximated using (Stratton 1941)

$$f_a = \sum_{i=1}^{3} \frac{\cos^2 \alpha_i}{1 + A_i \left[\left(\frac{\varepsilon_a}{\varepsilon^*} \right) - 1 \right]} \tag{6.3.1.8}$$

where α_i are the angles made by the ellipsoid axes a, b, c, and the applied field **E**. Following Reynolds and Hough(1957), for a random orientation of spheroids,

$$\cos^2 \alpha_a = \cos^2 \alpha_b = \cos^2 \alpha_c = \frac{1}{3}$$

and $A_i = 0.34$.

The only remaining parameter needed for full use of Eq. 6.3.1.7 is the dielectric constant of the solute molecule ε_a, which can be calculated using (Pethig 1979)

$$\frac{\varepsilon_a - 1}{\varepsilon_a + 2} = \frac{\overline{P}\rho}{\overline{M}} \tag{6.3.1.9}$$

where P (cm^{-3}) is the average molar polarization of the amino acids comprising the protein, ρ is the overall density (1.39 g/cm^3) (Pethig 1979), and M is the average Mw of the protein. Using the reported polarization values for the 20 amino acids and their Mw, we can obtain the average molar polarization for any protein provided that its amino acid sequence is known. Utilizing a protein databank such as the ExPASy proteomics web server ([SIB] 2006), amino acid sequences for the proteins used in this study were obtained and their average polarization, as well as their average MW, were calculated. Once ε_a and f_a are available and f_b is accurately approximated, ε_m is then easily calculated using Eq. 6.3.1.7.

6.3.2. Materials and Measurements

The frequency-dependent dielectric response of protein solution samples at 25^{o}C was measured between 5 MHZ and 1.8 GHz using a system consisting of an Agilent (formerly Hewlett Packard) 4291B impedance analyzer with a calibration kit (Agilent Technologies, Palo Alto, CA), an open-ended coaxial probe, a custom-built test cell, and a VWR Model 1157 programmable circulator (VWR Science Products, West Chester, PA). The impedance analyzer was connected through an IEEE-488 (GPIB) bus to a desktop computer used with custom-designed software (DMS 85070, Innovative Measurements Solutions) to control the impedance analyzer and log the measured data. The electrical conductivity was measured using a Cole-Parmer Model 19950 bench-top conductivity meter (Cole-Parmer Instrument Co., Vernon Hills, IL).

Six purified proteins were selected for this investigation: 1) ovalbumin (A2412) (≥98%, agarose gel electrophoresis), 2) bovine serum albumin (BSA) A7030 (≥98%, agarose gel electrophoresis), 3) BSA A7638 (≥99%, agarose gel electrophoresis), 4) lysozyme (L6876) (≈95%), 5) β-lactglobulin (BLG) L0130) (≥98%, PAGE), and 6) β-lactglobulin (BLG) JE 001-3-922) (≈ 95%). The first five proteins were purchased from Sigma-Aldrich, St. Louis, MO, and the sixth from Davisco Foods International, Le Sueur, MN. Selected proteins varied based on Mw, structure, primary function, and isoelectric point (pI). Samples were prepared by adding appropriate amounts of proteins to obtain a total of six levels of concentrations (wt/wt) into a fixed amount of double de-ionized water with average conductivity of 0.25 uS/cm at room temperature. Each sample was prepared in a 300 ml beaker and then divided into three 50 ml beakers to obtain three

measurement duplicates taken 2 min apart. Samples were maintained at a constant temperature (≈ 25°C), continuously stirred, and securely covered to prevent evaporation for no longer than 4 min. Reported data points are averages of three replicates in which the calculated standard deviation was less than 5% for all measurements. Error bars and statistical analysis are omitted in this treatment for clarity of presentation.

Ovalbumin is a phosphorylated-glycoprotein isolated from chicken egg white. The peptide portion of the molecule consists of 385 residues and has a Mw of 42.7 kDa. The carbohydrates and phosphate portions account for an additional 1428 and 160 g/mol respectively, giving a total Mw of 44.3 kDa. BSA (A7030) and (A7638) are a single polypeptide chain proteins of about 583 amino acids and no carbohydrates; at pH (5-7), it contains 17 intrachain bridges and 1 sulfhydryl group. The Molecular weight of BSA has frequently been cited as 66.1201 or 66.2672, but it was revised in 1990 to 66.430 kDa. A7030 is a globular protein wit purity >98% while A7638 is globulin-free with .99% purity. Lysozyme is a single polypeptide chain of about 129 amino acids cross-linked with 4 disulfide bridges and has a Molecular weight of about 14.307 kDa. protein content of lysozyme by UV absorbance is about 95% with the reminder being buffer salts such as sodium acetate and sodium chloride. BLG (L0130) contains β-lactoglobulins A and B with purity ~90% (PAGE), lyophilized powder with total Mw of 36.6 kDa. BLG (JE 001-3-922) is a native, undenatured 95% (98.3 dry basis) whey protein.

6.4. EXPERIMENTAL RESULTS AND DISCUSSION

6.4.1. Dielectric Constant and Loss Factor

At all six levels of concentrations, typical dispersion curves were obtained; ε' curves for 20 mg protein/g water are shown in Fig. 6.4.1.1. The resulting dispersion for all proteins can be divided into three distinct regions: 1) 5–50 MHz, 2) 50–1,000 MHz, and 3) 1,000–1,800 MHz. Region 1 represents dispersions due to relaxation of the protein molecules, traditionally termed β-dispersions (Oncley 1938, 1941, Grant et al. 1978). Previous investigations have placed this region's critical relaxation frequency (f_R) at about 2 MHz (Harvey and Hoekestra 1972), with a relaxation time (τ) at about 0.8 ns. Region 2 was the least explored region until new dispersions surfaced in the last couple of decades; namely, δ-dispersions attributed to either relaxation of bound water molecules (Feldman et al. 2003) or relaxation of mobile protons within macromolecules (Kirkwood and Shumaker 1952). Region 3 marks the onset of the well-established γ-dispersion for free water molecules (Tang et al. 2001).

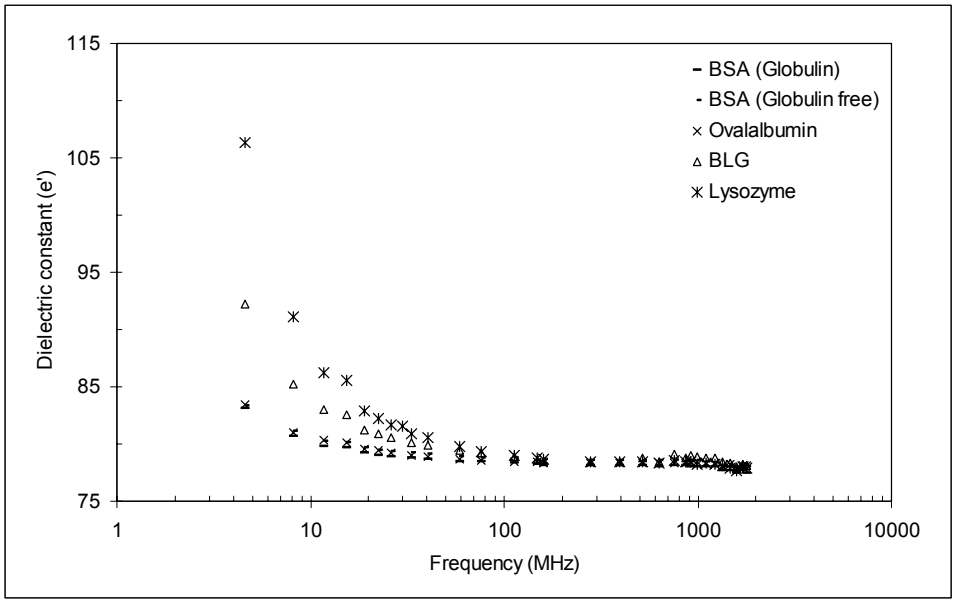

Figure 6.4.1.2. Dielectric dispersion curves for five different proteins at 20 mgprotein/gwater and 25°C.

In the dielectric heating range of the spectrum (1 MHz–1800 MHz), the significance of energy absorption and dissipation is generally overlooked since they are associated with low frequencies compared to the critical relaxation frequency of water molecules (20 GHz at 25°C) (Von Hippel 1995) which has a dielectric loss close to zero at lower frequencies. However, when considering the product of *f* and ε" (e.g., heating factor) in the power dissipation equation (Eq. 6.4.1.1) instead of *f* alone, the contribution of the ε" from the solute molecules becomes significant since its values are much larger than those of water, as indicated in Fig. 6.4.1.2. In other words, the heating factor for the solute molecules at 5 MHz is approximately 5.0 x 10^8 (100 x 5 MHz) compared to that of water at the same frequency 1.0 x 10^5 (0.02 x 5 MHz), which is a 5,000-fold increase. This is of paramount importance in dielectric heating and drying of biological materials, especially for the newly explored RF technology for food drying, pasteurization, and sterilization. RF system engineering designs are based almost exclusively on the moisture

content of the material. Similarly, theoretical treatments discuss and interpret the thermal generation within the material that is to be dielectrically heated from the context of water molecule dipolar rotation.

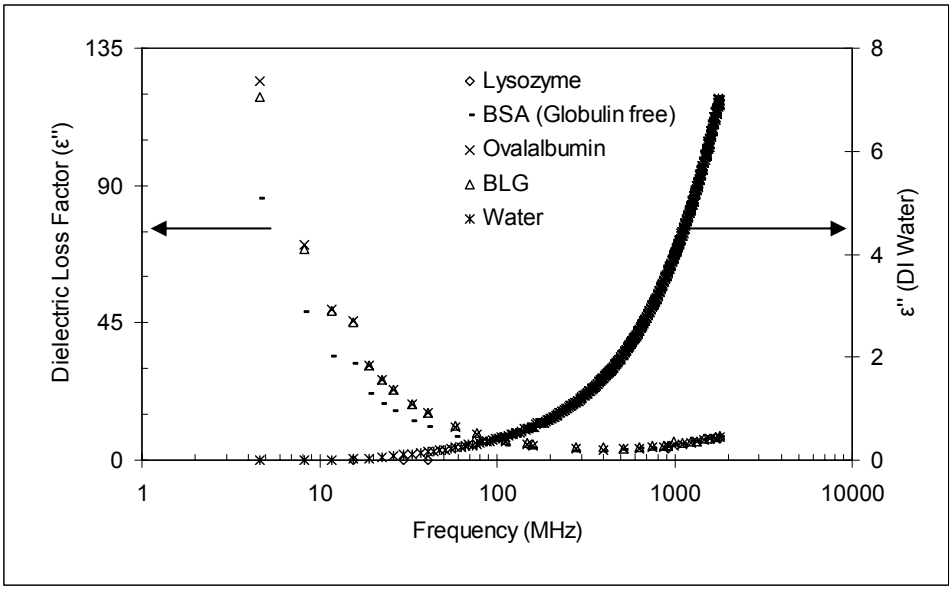

Figure 6.4.1.3. Dielectric loss of selected proteins (20 mg protein/ml) compared to the loss of pure water at 25^{o}C.

No matter how high the moisture content of a biological material gets, processing it at low frequencies so that other molecules relax before water molecules results in much of the heat being generated by the solutes rather than water. Therefore, accounting for the absorption by solutes in a biological mixture becomes essential for adequate understanding of the underlying mechanism controlling the dielectric behavior of the entire mixture. Furthermore, quantification of their contribution to the overall dielectric

properties of the mixture is necessary for proper system design and prediction and modeling of mixture properties.

Quantifying the contribution of protein constituents to the overall absorption of the system reveals that each protein molecule absorbs an average 3.5–10% that of free water molecules (South and Grant 1974, Schutz and Warshel 2001). Theoretical calculations of the local ε' of individual proteins from their amino acid makeup resulted in an average value of 2.7 for the ε' in a static field (also in alternating fields), as shown in Table 6.4.1.1.

Table 6.4.1.1. Calculated polarization and dielectric constant (ε') of individual proteins from their amino acid composition.

Molecule	**Avg. Mw†**	**Avg. Polarization** (Pethig 1979)	**ε'**
Water	18.00	260	65.50
Bovine Serum Albumin	3516	917	2.66
Ovalbumin	2170	567	2.71
B-Lactglobulin	2019	526	2.70
Lysozyme	816	213	2.70

†The average molecular weights for proteins are computed by taking the average of the total amino acid composition rather than the summation (i.e., Mw (kDa) = (∑number of individual amino acid x amino acid Mw)/total number of amino acids), as commonly reported in the literature.

Another measure of the overall dielectric dispersion and absorption of solutes in a solvent that is commonly used in studies of protein solutions is the dielectric decrement (Δε') and/or absorption increment (Δε") (Grant et al. 1968). Δ is a measure of the dielectric property deviation from pure water values at each frequency (i.e., $\Delta = \varepsilon_{mixture} - \varepsilon_{water}$). This measure is a simplified indicator of the overall dielectric behavior of a mixture in an EM field, for it shows the general trend of energy absorption and the effect of the contribution by each component of a mixture, particularly binary mixtures where the dielectric properties of one of the components is well-defined.

Δ can be negative or positive. Negative values simply indicate that the solvent (water) is absorbing a higher fraction of the EM than that of the solutes, whereas positive values signify the opposite. Additionally, Δ shows the effect of increasing the concentration of the solutes on the overall dielectric properties of the mixture in which increasing solute content appears to continuously increase both dielectric properties at low frequencies and decrease the properties as frequency is increased (Fig. 6.4.1.3).

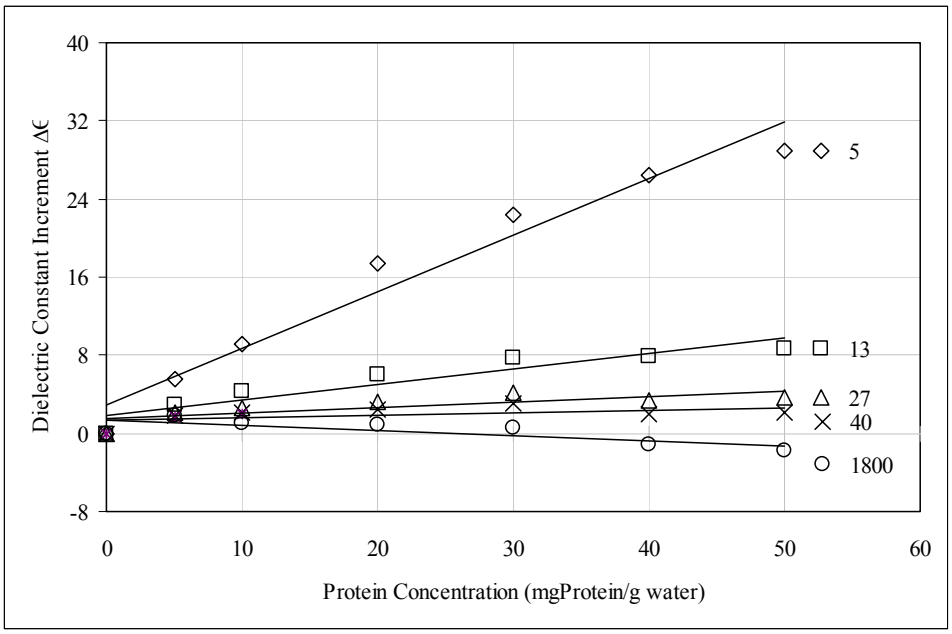

Figure 6.4.1.4. Protein concentration effect on the solution's dielectric dispersion decrements at 5, 13, 27, 40, and 1,800 MHz frequencies (all measurements at 25^{o}C).

Dielectric dispersion decrements (Δε') and absorption increments (Δε") also prove more helpful in providing significant effects of solute structure and size on the overall dielectric behavior of macromolecules. From Table 6.4.1.2 one can observe that as the

molecular size increases, its Δε' and Δε" decrease in agreement with the molecular rotation hypothesis. That is, as long as the macromolecule is capable of following the alternating EM field, its dispersion and absorption become solely dependent on its ability to overcome the viscous forces exerted on it by the surrounding molecules. Therefore, the larger the molecule, the slower its rotation, and consequently, the lower its contribution to the overall dielectric mechanism of the entire mixture. Table 6.4.1.2 also indicates that the largest molecule (BSA) contributed the least to the dispersion and absorption of the mixture relative to those smaller molecules.

Moreover, closer examination of the Δ for globulin versus globulin-free proteins reveals that alterations of solute physical structure (i.e., removal of globulins) directly influences the overall dielectric behavior of the mixture. Table 6.4.1.2 demonstrates that non-globulin proteins have lower capability in energy dispersion and absorption than globular ones. This is also in accordance with the dielectric theory interpretation in which increasing protein surface area negatively influences the dielectric behavior of molecules when placed in an alternating field (Gabler 1978). This is of interest in thermal processing of foods with high protein content in which denaturation (unfolding) of proteins at high temperatures eventually results in altering the processing parameters of the applied EM energy. When examining the temperature effect on the dielectric mechanism of egg protein, Bircan and Barringer (2002) observed that at about 80^{o}C, egg ovalbumin denatured, causing a decrement in both ε' and ε" of the protein.

Table 6.4.1.2. Dielectric dispersion decrements (Δε') and absorption increments (Δε") for selected proteins at six levels of concentrations and 25°C.

Dielectric increments/decrements of protein solutions anlysis													
Beta-Lactglobulin (Davisco Co.) |		Frequency (MHz)											
		5 MHz		13		27		40		915		1800	
mg/g H_2O	σ (μS/cm)	Δε'	Δε"	Δε'	Δε"	Δε'	Δε"	Δε'	Δε"	Δε'	Δε"	Δε'	Δε"
0	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	129.00	5.60	47.93	2.85	18.32	2.07	9.02	1.86	6.20	1.68	0.51	1.79	0.74
10	244.67	9.15	76.44	4.28	35.05	2.54	17.21	2.11	11.91	1.94	1.00	0.97	0.51
20	476.00	17.41	177.22	6.09	67.27	3.23	33.11	2.40	22.77	0.65	1.39	0.89	1.15
30	639.00	22.36	240.38	7.72	90.78	4.13	44.70	3.02	30.86	0.51	2.13	0.54	1.62
40	829.00	26.47	311.05	7.86	117.22	3.33	57.68	1.96	39.78	-1.22	2.31	-1.16	1.11
50	975.00	29.00	359.16	8.75	135.38	3.66	66.52	2.14	45.80	-1.68	2.89	-1.75	1.65
Beta-Lactglobulin (Sigma-Aldrich Co.)													
0	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	94.50	5.16	34.48	2.40	13.16	1.92	6.47	1.80	4.55	2.31	0.74	2.19	0.66
10	174.30	7.11	68.66	1.60	26.20	0.41	12.94	0.08	8.99	0.02	0.78	-0.12	0.47
20	311.00	14.25	118.82	4.64	45.29	2.53	22.42	1.93	15.56	1.17	1.31	0.90	0.97
30	446.00	18.72	167.10	5.65	63.47	2.77	31.38	1.95	21.75	0.45	1.68	0.18	1.20
40	515.00	22.25	208.69	6.15	79.13	2.60	39.03	1.61	26.95	-0.43	1.92	-0.65	1.29
50	584.00	24.51	239.16	6.14	90.64	2.08	44.67	0.95	30.83	-1.38	2.11	-1.60	1.20
Bovine Serum Albumin (Globulin-Free)													
0	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	68.80	3.22	24.61	2.25	9.15	2.03	4.50	1.98	3.09	1.78	0.43	2.04	0.55
10	123.20	4.13	46.36	2.38	17.16	1.94	8.38	1.83	5.76	1.52	0.62	1.64	0.58
20	237.00	5.27	85.48	2.21	31.49	1.42	15.36	1.17	10.54	0.59	0.85	0.69	0.66
30	331.00	6.65	121.44	2.23	44.68	1.17	21.77	0.84	14.91	-0.07	1.10	0.13	0.76
40	412.50	7.60	152.46	1.97	56.04	0.69	27.26	0.28	18.65	-0.84	1.30	-0.63	0.86
50	494.00	8.29	180.80	1.46	66.37	-0.02	32.22	-0.44	22.03	-1.78	1.41	-1.59	0.76
Bovine Serum Albumin (Globular)													
0	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	65.70	1.91	22.85	0.97	8.47	0.80	4.13	0.74	2.81	0.81	0.40	1.04	0.50
10	119.10	3.33	42.73	1.58	15.85	1.16	7.72	1.03	5.29	0.88	0.61	1.02	0.68
20	221.00	5.05	80.02	1.71	29.55	0.97	14.42	0.73	9.87	0.17	0.93	0.23	0.88
30	314.00	6.05	114.50	1.29	42.13	0.26	20.53	-0.08	14.06	-0.91	1.17	-0.82	0.95
40	400.00	7.49	145.92	1.38	53.72	0.07	26.16	-0.37	17.92	-1.56	1.42	-1.52	1.10
50	477.00	7.12	173.12	-0.02	63.65	-1.55	30.98	-2.04	21.23	-3.50	1.55	-3.54	0.99
Ovalalbumen													
0	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	105.80	4.67	40.96	3.16	15.53	2.57	7.75	2.34	5.37	2.29	0.63	2.82	0.86
7	122.20	4.67	47.80	3.10	18.04	2.48	8.95	2.25	6.17	2.13	0.71	2.61	0.83
8	145.70	4.46	56.27	2.75	21.12	2.07	10.46	1.82	7.21	1.71	0.68	2.07	0.84
10	179.80	4.92	69.33	2.96	25.86	2.22	12.75	1.96	8.75	1.79	0.68	2.29	0.66
13	231.00	5.03	88.42	2.68	32.77	1.88	16.03	1.59	10.93	1.18	0.80	1.75	0.76
20	349.00	5.43	124.41	2.21	45.83	1.26	22.28	0.91	15.23	0.40	0.91	0.85	0.74
Lysozyme													
0	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	424.00	9.81	150.40	3.63	55.26	2.42	26.76	2.06	18.25	1.67	1.24	1.84	1.21
10	724.00	17.11	281.97	5.41	103.43	3.04	49.93	2.38	33.94	1.15	1.98	1.34	1.50
20	1366.00	28.31	480.85	7.63	176.13	3.63	85.07	2.57	57.90	0.55	3.21	0.67	2.09
30	1834.00	39.71	675.48	9.48	246.56	4.01	118.93	2.60	80.87	-0.22	4.35	-0.13	2.66
40	2260.00	50.73	850.35	11.07	309.30	4.26	149.06	2.56	101.28	-0.96	5.35	-0.92	3.18
50	2690.00	53.14	945.50	7.69	343.45	-0.01	165.61	-1.92	112.55	-5.46	5.66	-5.46	3.00

Calculated values of the dielectric constant using the mixture equation (Eq. 6.2.7) resulted in comparable values at frequencies close to 915 MHz, suggesting that the optimum electric field absorption may take place within the 900–1,000 MHz range of the spectrum (Table 6.4.1.3). This is evident from the behavior of the ε' at low frequencies versus high frequencies in which it continuously exceeded the calculated values at low frequencies (<900 MHz) and produced lower values at higher frequencies (>1,000 MHz) as shown in Fig. 6.4.1.4. However, this interpretation is dependant upon the accuracy of the assumptions made in deriving the mixture equation; namely, electric field distribution, solute structure, and intermolecular interactions between solutes and solvent molecules.

Table 6.4.1.3. Experimental vs. calculated dielectric constants of protein solutions using simplified mixture theory for 915 MHz at six concentration levels and 25°C.

	β-LG (Davisco Co.)		β-LG (Sigma Co.)		BSA (GF)		BSA (G)		Ovalbumin		Lysozyme	
Conc. (wt/wt)	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$	$\epsilon'_{experimental}$	$\epsilon'_{calculated}$
5	79.56	77.81	80.19	77.81	79.66	77.81	78.68	77.81	80.17	77.80	79.54	77.81
10	79.82	77.68	77.90	77.68	79.39	77.68	78.76	77.68	80.00	77.77	79.03	77.68
20	78.53	77.42	79.05	77.42	78.46	77.42	78.05	77.42	79.59	77.74	78.42	77.42
30	78.39	77.16	78.33	77.16	77.81	77.16	76.97	77.16	79.67	77.68	77.66	77.16
40	76.65	76.91	77.45	76.91	77.04	76.91	76.31	76.91	79.06	77.60	76.91	76.91
50	76.19	76.66	76.50	76.66	76.09	76.66	74.38	76.66	78.28	77.42	72.42	76.66

Although the foregoing discussion was concerned only with the real part (ε') of the complex relative permittivity (ε^*_r), similar analysis can be performed for the imaginary part (ε") provided that the loss from each component in the mixture is closely approximated. Prior efforts to approximate the loss contribution by solute molecules in

model mixtures unfortunately deviated appreciably from the experimental data and reasonable agreement was obtained only for very dilute solutions (Hasted 1973). One of the primary reasons for the deviation of the experimental data from the theoretical treatments appears to lie in the limited frequency range utilized for the experiments. Measurements of either the real or imaginary parts over wider frequency spectra may result in better agreement by using Kramers-Kronig relations:

$$\varepsilon'(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega'\varepsilon''(\omega')}{\omega'^2 - \omega^2} d\omega' \tag{6.4.1.1}$$

and

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\varepsilon'(\omega')}{\omega'^2 - \omega^2} d\omega' \tag{6.4.1.2}$$

A final observation to be noted here is the influence of the solute content on the dispersion mechanism as a function of frequency. Increasing protein content resulted in a progressive increase in dispersion at low frequencies and lower dispersion at higher frequencies (Fig. 6.4.1.7). This behavior was not as significant in the calculated values perhaps because the mixture equation excluded the fluctuation effect due to the alternating EM field. This influence may become more pronounced as the system temperature changes since dielectric properties are a strong function of field frequency; regardless, it is an opportunity for further research into the dielectric pasteurization and sterilization of food materials at elevated temperatures.

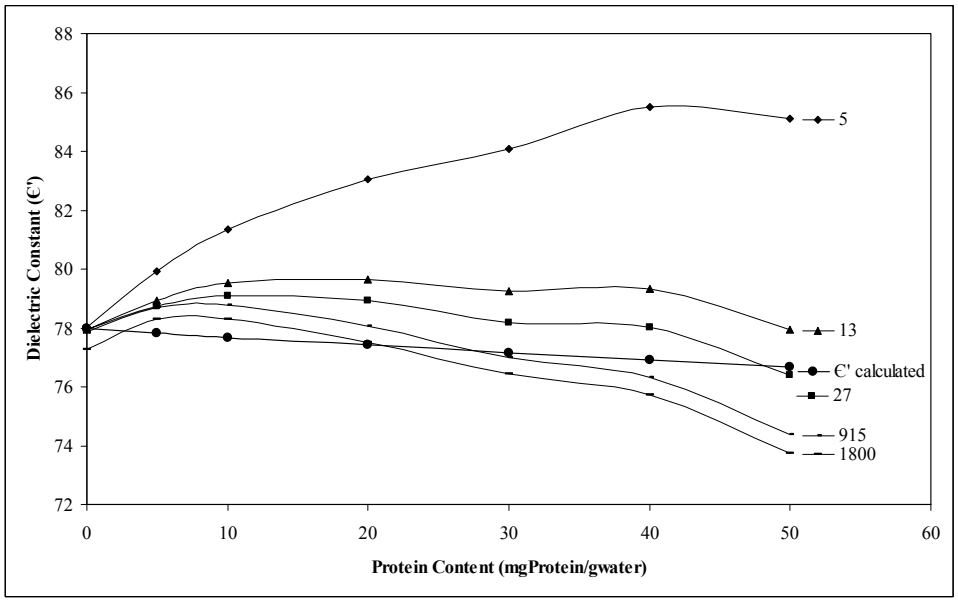

Figure 6.4.1.5. Experimental vs. calculated dielectric constant as a function of protein concentration and field frequency at 25°C.

6.4.2. Electrolyte Content

To examine the influence of electrolytes on the solutions' overall ε', experimental measurements of electrical conductivity (σ, μS/cm) were conducted on highly purified (≥99%; Sigma-Aldrich Co.) β-lactoglobulin solutions and food-grade (≥95%; Davisco Foods Intl. Inc.) β-lactoglobulin solutions (Fig. 6.4.2.1). The corresponding dielectric constants and loss factors were also measured (Table 6.4.2.1), along with estimation of the contributions from exiting electrolytes using Eq. (3.2.3) at 27 MHz and 1,800 MHz. The resulting elevation due to impurities was approximately 1.2% for the dielectric constant at 27 MHz, and about 0.07% for the 915 MHz frequency. Debye (1929) calculated a potassium chloride (KCl) solution at 0.7% for every millimole of salt per

liter, which is a very small effect, especially when considering the concentrations used in the current study of proteins and carbohydrates.

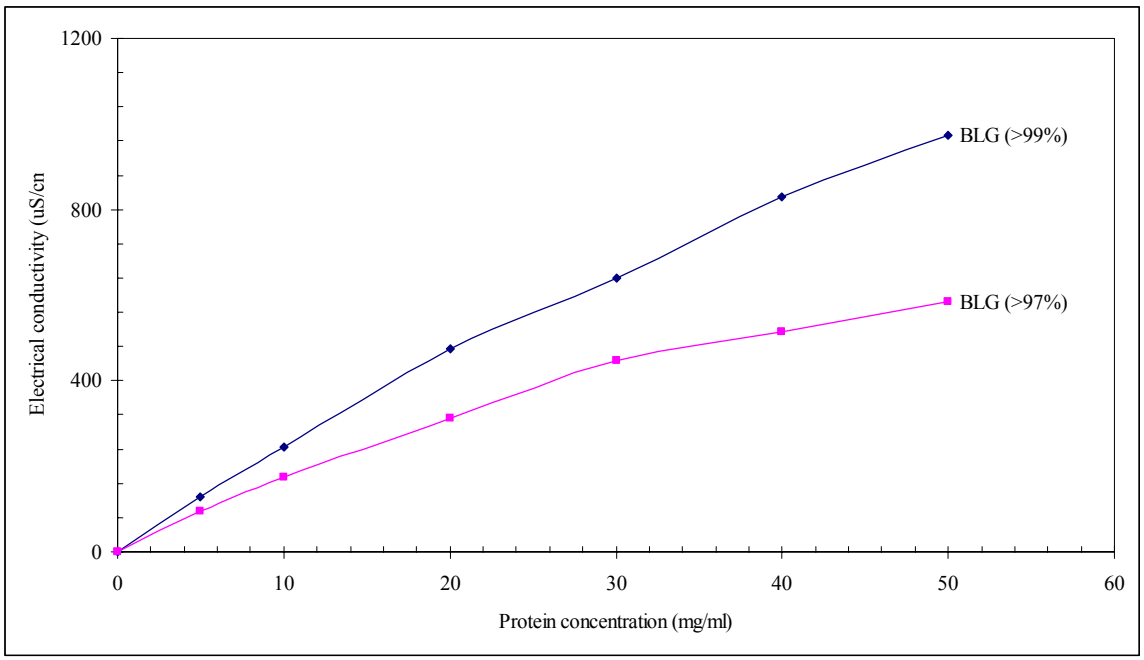

Figure 6.4.2.1. Electrical conductivity of β-lactoglobulin solutions at 23°C, along with the influence of electrolytes impurities.

Table 6.4.2.1. Electrical conductivity and dielectric properties of β-lactoglobulin solutions at various concentrations at 23°C.

Beta-Lactglobulin (Davisco Co.)		Frequency (MHz)					
		27		915		1800	
mg/g H_2O	σ (μS/cm)	Є'	Є''	Є'	Є''	Є'	Є''
0	0.37	78	0.09	78	3.61	77	6.97
5	129.00	80.01	9.11	79.56	4.13	79.06	7.71
10	244.67	80.48	17.30	79.82	4.61	78.24	7.49
20	476.00	81.17	33.19	78.53	5.00	78.15	8.13
30	639.00	82.07	44.79	78.39	5.74	77.80	8.59
40	829.00	81.27	57.77	76.65	5.92	76.10	8.08
50	975.00	81.60	66.61	76.19	6.50	75.52	8.63
Beta-Lactglobulin (Sigma-Aldrich Co.)							
		27		915		1800	
gBLG/g H_2	σ (μS/cm)	Є'	Є''	Є'	Є''	Є'	Є''
0	0.37	78	0.09	78	3.61	77	6.97
5	94.50	79.86	6.56	80.19	4.35	79.45	7.63
10	174.30	78.35	13.03	77.90	4.39	77.15	7.44
20	311.00	80.47	22.51	79.05	4.92	78.16	7.94
30	446.00	80.71	31.47	78.33	5.29	77.44	8.17
40	515.00	80.54	39.12	77.45	5.53	76.61	8.26
50	584.00	80.02	44.76	76.50	5.72	75.67	8.17

Although the effect of electrolytes at small concentrations on a solution's dielectric constant is fairly small and can be safely neglected, the effect on the dielectric loss can be significant and must be accounted for, especially at RF frequencies (see Table 6.4.2.2). This is because at low frequencies (i.e., <400 MHz), the ionic conduction contribution to the overall dielectric loss can be far greater than the dipolar rotation contribution. Elevation of dielectric loss results from the addition of conductive charge carriers that are able to migrate by electrophoresis in the direction opposite to the polarity of the applied field. To correctly quantify the amount of dissipated power (i.e., the

specific electrical energy conversion to heat) within the dielectrically heated product, measured values of the dielectric loss need to be corrected for the ionic conductivity of the solution. This can be accomplished with the following expression (Grant et al.1978):

$$\varepsilon_t'' = \varepsilon_d'' + \frac{\sigma}{2\pi f \varepsilon_0} \qquad (6.4.2.1)$$

where ε_t'' is the total dielectric loss, σ is the electrical conductivity (S/m), ε_o is the free space permittivity (8.854×10^{-12} F/m), and f is the EM wave frequency (Hz). Furthermore, if the electrical conductivity is assumed to be frequency-independent (this is a safe assumption for low frequencies such as RF, but may not be at MW frequencies), then the ε" of an electrolyte-free solution can be accurately calculated. Examination of Table 6.4.2.2 reveals that the dielectric loss due to ionic contribution is about 85% of the total solution's dielectric loss for the 27 MHz frequency, and 5% of the total loss at the 915 MHz frequency, an increase of approximately 1,500 times.

Table 6.4.2.2. Measured dielectric loss for β-lactoglobulin solutions vs. calculated dielectric loss due to ion migration; all measurements at 23°C.

Beta-Lactglobulin (Davisco Co.) |		Frequency (MHz)					
		27		915		1800	
mg/g H_2O	σ (μS/cm)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)
0	0.37	0.089	0.025	3.61	0.001	6.97	0.000
5	129.00	9.105	8.588	4.13	0.253	7.71	0.129
10	244.67	17.296	16.289	4.61	0.481	7.49	0.244
20	476.00	33.195	31.690	5.00	0.935	8.13	0.475
30	639.00	44.790	42.542	5.74	1.255	8.59	0.638
40	829.00	57.768	55.191	5.92	1.629	8.08	0.828
50	975.00	66.612	64.911	6.50	1.915	8.63	0.974
Beta-Lactglobulin (Sigma-Aldrich Co.)							
		27		915		1800	
mgBLG/g H_2O	σ (μS/cm)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)	ϵ_t"(measured)	$\epsilon\sigma$"(calculated)
0	0.37	0.09	0.025	0.09	0.001	3.61	0.000
5	94.50	6.56	6.291	6.56	0.186	4.35	0.094
10	174.30	13.03	11.604	13.03	0.342	4.39	0.174
20	311.00	22.51	20.705	22.51	0.611	4.92	0.311
30	446.00	31.47	29.693	31.47	0.876	5.29	0.445
40	515.00	39.12	34.287	39.12	1.012	5.53	0.514
50	584.00	44.76	38.880	44.76	1.147	5.72	0.583

6.5. SUMMARY AND CONCLUSIONS

Dielectric heating of foods and other biomaterials has great potential for providing rapid, safe, and high quality products once issues related to non-uniformity, edge heating, and runaway heating are resolved. Resolving these issues and others seem to lie within gaining a comprehensive understanding of the nature of the interactions between treated products and the applied energy. Interactions between treated materials and EM energy are molecular in nature and governed primarily by two parameters, ε' and ε", generally termed dielectric properties.

The primary objective of this study was to provide explanation and analysis of the interactions between common food proteins and EM energy fields. Efforts were directed towards accurately quantifying the amount of EM absorbed by individual proteins and

utilizing the results in a simplified mixture equation. The dielectric contribution from proteins was computed from their amino acid sequence using computed average molecular polarization and Mw. Results showed that proteins in solutions on average absorb about 3.5–10% of applied energy. Computation of ε' for the six selected proteins resulted in values between 2.66 and 2.72.

Increasing field frequency and/or protein concentration caused the absorption of EM to shift from being protein-dominated to solvent-dominated. Experimental data indicates a possibility of changing the point where the absorption shifts from being solute-dominated to a solvent-dominated mechanism in terms of frequency and concentration. Further investigation should yield the frequency and concentration at which the absorption mechanism makes the transition.

Dielectric increments and decrements can indicate the overall dielectric mechanism of the solution and its effects due to processing and material properties. Solute physical size and structure appeared to influence the overall absorption of the mixture by continuously decreasing the dielectric properties as either one increased. This result conforms to the dielectric theory interpretation of the overall mechanism being directly influenced by the viscous forces within a medium in which factors causing an increase in viscosity generally depress its overall dielectric properties.

Finally, the mixture equation (Eq. 6.3.1.7) appeared to predict the dielectric constant (ε'), and consequently ε" via Kramers-Kronig relations, at frequencies close to 915 MHz. The prediction capability of the mixture equation may further be improved if impurities introduced with samples are limited or their contribution to the ionic

translation mechanism is accurately quantified, especially at the lower end of the spectra. At higher frequencies, prediction of dielectric properties should be limited to contributions from free water molecules alone, provided that its amount is accurately determined. Examination of loss due to the presence of impurities (e.g., electrolytes) revealed that 85% of the dielectric loss at 27 MHz was due to ionic conduction, while this effect accounted only for 16% of the loss at 915 MHz.

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CHAPTER SEVEN

DIELECTRIC PROPERTIES OF FOOD CARBOHYDRATE-PROTEIN AQUEOUS MIXTURES

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7.1. ABSTRACT

The dielectric properties of protein-carbohydrate aqueous mixtures were investigated in the 10–1,800 MHz frequency range of the electromagnetic (EM) spectrum. Measurements were conducted using the coaxial probe method at 23^{o}C. β-lactoglobulin, lysozyme, glucose, fructose, and sucrose were used to quantify their contribution to the mixture's overall dielectric properties. The influence of solute concentrations, molecular structure and size, and field frequency on the mixture's dielectric constant and loss factor were examined. Rayleigh, Böttcher, and Berentsveig mixture models were used to predict the mixtures' dielectric constants and results were compared to the experimental data. Model results agreed fairly well with the experimental data, except for the three-component mixture result obtained using the Rayleigh model, which under-predicted the mixture's dielectric constant by almost 45% (37 vs. 66).

7.2. INTRODUCTION

Dielectric heating of foods using microwave (MW) ovens in homes is a success story, especially in developed countries, with almost 100% penetration in the USA, Japan, and Australia, and over 80% in the UK and Nordic countries (Ryynänen 1995). Although the number of household MW ovens has increased rapidly, with nearly 25 million units produced annually, their commercial use is limited to reheating and tempering foods rather than cooking (Gunasekaran 2002). The inability to thoroughly cook food products using MW ovens without causing quality losses is a major safety concern, especially for the heavily regulated food processing industry. This concern has translated into a much slower growth in industrial applications of dielectric heating systems (e.g., 1,000 globally as of 2002) compared to domestic (Ryynänen 2002).

Scientists and engineers involved in research and development of electromagnetic (EM) energy applications via MW and radio frequency (RF) ovens primarily attribute this slow growth to the uneven heating profile of processed foods. Additionally, issues related to their inability to brown foods, the presence of cold spots at unpredictable locations, edge heating, runaway-heating, sudden bursting (solid and semi-solid products), and recursive boiling (liquids) exacerbate the problems associated with dielectric processing of foods commercially. These difficulties stem from a lack of understanding of the underlying interaction mechanisms between the material and the applied EM energy.

Interaction between the material and the applied EM energy is chiefly controlled by EM properties, especially the dielectric properties of the food. These properties are the principal parameters that determine the coupling and distribution of EM energy

throughout the product during dielectric heating (Tang et al. 2001). Dielectric properties are normally described in terms of their complex relative permittivity, ε_r^*:

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \tag{7.2.1}$$

where $j=\sqrt{-1}$. The real part of the relative complex permittivity, ε'_r, known as the dielectric constant, describes the ability of a material to store energy in response to an applied electric field. The imaginary part of the relative complex permittivity, ε''_r, known as the loss factor, describes the ability of a material to dissipate energy in response to an applied electric field, which typically results in heat generation (Mudgett 1985).

Accurate data for the dielectric properties of biological materials is necessary for successful and efficient application of EM energy for dielectric heating, which inevitably includes equipment design. Reliable determination and measurement of these properties is a crucial challenge for scientists and engineers working in the area of dielectric heating due to the complex nature of biological materials. Foods are biologically active complex materials comprised of numerous constituents commonly categorized via proximate analysis into four main components: carbohydrates, proteins, lipids, and water. Consistent measurements and reliable prediction of food dielectric properties can be obtained when precise account of the dielectric behavior of the individual components comprising the food is readily available and soundly justified. Although an extensive database of dielectric parameters is now available for a variety of foods and biological materials (Tinga and Nelson 1973, Stuchly 1980, Kent 1987, Thuéry and Grant 1992, Datta et al. 1994, Tang et al. 2001), paucity still exists in the understanding of the mechanisms

underlying the causes and sources contributing to the variability and unpredictability in the reported measured values under different common conditions and system variables.

To address this research need, the current investigation of the dielectric properties of food carbohydrate-protein aqueous mixtures provides an analysis and quantification of the dielectric properties of common constituents in foods for modeling purposes. These models can then be extended to more natural complex food materials. The primary objective of this effort is to explore the possibility of constructing a mathematical model capable of predicting the overall dielectric properties of basic food constituents. When successful, these models can be further modified to predict the dielectric properties of naturally occurring food mixtures.

7.3. METHODS AND MATERIALS

7.3.1. Methods

In mixture models, the dielectric properties of a material are commonly expressed in terms of the dielectric properties of each of the individual components comprising the mixture and their corresponding volume fractions. Several reviews of dielectric mixture models have been published in the literature (Tinga and Nelson 1973, Wang and Schmugge 1980, Dobson et al. 1985, Thakur et al. 1999, Yaghmaee and Durance 2002), along with the existing mixture models (Wang and Schmugge 1980, Shivola 1999). In this study, we utilize only three models common to media with high moisture content: 1) the classical Rayleigh model, 2) the Böttcher equation (Böttcher 1952) generalized by

Boersma and Van Turnhout (1999) for multicomponent systems, and 3) the Berentsveig model. Parameters used in the models are reported in Table 7.3.1.1 below.

1) The Rayleigh Model

The Rayleigh model (Tinga and Nelson 1973) is given by

$$\frac{\varepsilon_m - 1}{\varepsilon_m + 2} = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} v_1 + \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} v_2 + \frac{\varepsilon_3 - 1}{\varepsilon_3 + 2} v_3 \qquad (7.3.1.1)$$

where ε_m is the mixture dielectric constant and ε_1, ε_2, v_1, and v_2 are the dielectric constant and volume fractions of components (1), (2), and (3), respectively. This model can be extended to an *n*-component system.

2) The Böttcher Model

The Böttcher model (Thakur et al. 1999) is given by

$$\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} v_1 + \frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 + 2\varepsilon_m} v_2 + \frac{\varepsilon_3 - \varepsilon_m}{\varepsilon_3 + 2\varepsilon_m} v_3 = 0 \qquad (7.3.1.2)$$

where ε_1, ε_2, ε_3, and ε_m are the dielectric constants of solutes 1, 2, and 3; and v_1, v_2, and v_3 are the volume fraction of components 1, 2, and 3. When dealing with a multi-component system, Eq. 7.3.1.2 can be rewritten as (Boersma and Van Turnhout 1999)

$$\sum_{i=1}^{n} \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} f_i = 0 \qquad (7.3.1.3)$$

where ε_m is the dielectric constant of the mixture, ε_i is the dielectric constant of the n component, and f_i is the volume fraction of the *ith* component.

3) The Berentsveig Model

The Berentsveig formula (Tinga and Nelson 1973) has the form

$$\varepsilon_m = \varepsilon_{avg} + \frac{\sum_{i=1}^{n} f_i \frac{\varepsilon_i - \varepsilon_{avg}}{\varepsilon_i + 2\varepsilon_{avg\ i}}}{\sum_{i=1}^{n} f_i \frac{1}{\varepsilon_i + 2\varepsilon_{avg}}} \qquad (7.3.1.4)$$

where ε_{avg} is the average dielectric constant, ε_i is the dielectric constant of component i, and ε_{avg} is defined by

$$\varepsilon_{avg} = \sum_{i=1}^{n} f_i \varepsilon_i \qquad (7.3.1.5)$$

Table 7.3.1.1. Values for parameters used in mixture models, where v_i and ε_i are the volume faction and dielectric constant of component i in the mixture, respectively, and ε_i is the calculated value from measurements conducted on aqueous solutions for each component at 20% (wt/wt) concentrations and 20°C.

		β-lactoglobulin-glucose-lysozyme		β-lactoglobulin-glucose		β-lactoglobulin-sucrose		B-lactoglobulin-fructose	
Frequency	Component	v^b_i	ε_i^a	v^b_i	ε_i^a	v^b_i	ε_i^a	v^b_i	ε_i^a
27 MHz	Lysozyme	0.004	2.73	0	NA	0	NA	0	NA
	Sugar	0.042	41	0.14	41	0.14	55	0.14	55
	Water	0.918	78	0.86	78	0.86	78	0.86	78
915 MHz	Lysozyme	0.004	2.73	0	NA	0	NA	0	NA
	Sugar	0.042	38.33	0.14	38.33	0.14	44.47	0.14	49.14
	Water	0.918	77.58	0.86	77.58	0.86	77.58	0.86	77.58

[a]The dielectric constants for the sugars were calculated using the Böttcher model for a two-component system, whereas for lysozyme the value was obtained from the molecular model discussed in chapter 6.
[b]Volume fractions were computed from the weight fractions using 1.39 g/cm^3 for protein density and 0.54 g/cm^3 for sugars.

Mixtures were prepared by dissolving required quantities of carbohydrates and proteins in double-deionized-distilled (DDD) water to obtain a total of five levels of concentrations (7, 13, 18, 23, 27% wt/wt). Each sample was prepared in a 300 ml beaker, and then divided into three 50 ml beakers to obtain three measurement duplicates taken 2 min apart. Samples were maintained at a constant temperature (≈ 25^{o}C), continuously stirred, and securely covered for no longer than 4 min to prevent evaporation. Measurements were repeated three times, and reported data points are averages of 9 points (3 x 3). The DDD water's electrical conductivity (σ) varied from 17.0–23.0 μS/cm between runs.

The measurement system consisted of an Agilent 4291B impedance analyzer (Agilent Technologies, Palo Alto, CA), an open-ended coaxial probe (Hewlett-Packard 85070B), a custom-built test cell (Wig 2001), and a VWR Model 1157 programmable circulator (VWR Science Products, West Chester, PA). The impedance analyzer was connected through an IEEE-488 (GPIB) bus to a desktop personal computer used with custom-designed software DMS 85070 (Innovative Measurements Solutions, Inc.) to control the impedance analyzer and log the measured data. The impedance analyzer was calibrated by first warming for at least 30 min before measurements were conducted per the recommendations of the manufacturer, then by using the 4219B calibration kit. The kit included four calibration standards: an open, a short, a 50X load, and a low-loss capacitor. The testing probe was calibrated using an 85070B dielectric probe kit that

included a short circuit (a gold-plated precision shorting block), an open circuit (air), and a known load (pure water at 25°C). The electrical conductivity was measured using a Cole-Parmer Model 19950 bench-top conductivity meter (Cole-Parmer Instrument Co, Vernon Hills, IL).

7.3.2. Materials

Three sugars (glucose, fructose, and sucrose, Sigma-Aldrich Chemicals; St. Louis, MO), and two purified proteins (lysozyme and β-lactglobulin, BLG, JE001-3-922) were selected for this investigation. The lysozyme was purchased from Sigma-Aldrich, St. Louis, MO and the BLG from Davisco Foods International, Le Sueur, MN. Lysozyme is a single polypeptide chain of about 129 amino acids cross-linked with four disulfide bridges and has a molecular weight (Mw) of about 14.307 kDa. The protein content of lysozyme by UV absorbance is about 95%, with the reminder being buffer salts such as sodium acetate and sodium chloride. BLG L0130 contains β-lactoglobulins A and B with ~90% (PAGE) purity, a lyophilized powder with a total Mw of 36.6 kDa. BLG JE 001-3-922 is a native, undenatured 95% (98.3% dry basis) pure whey protein.

7.4. RESULTS AND DISCUSSION

7.4.1. Dielectric Constant

The dielectric constant (ε') as a function of field frequency for 20% (g_{solute}/ml) β-lactoglobulin-sugar (6:1 ratio) solutions at 20^{o}C is shown in Fig. 7.4.1.1. Examination of the data depicted in Fig. 7.4.1.1 reveals that the addition of sugars to the protein solution

caused a significant depression of the overall ε' of the solution. A considerable difference was observed for the ε' as a function of frequency when lysozyme was introduced into the mixture, as shown in Fig. 7.4.1.2. Although the magnitude of ε' varied significantly with changes in solute concentrations, the overall trend with respect to the field's frequency remained consistent. Figure 7.4.1.3 represents the dielectric mechanism for the β-lactoglobulin-glucose aqueous solution, which closely resembles mechanisms exhibited by the other protein-sugar solutions. A correlation between the decrements of the solution ε' and the structure of the sugars is also evident, in which the simple sugars caused a larger depression than the complex sugar. This behavior further supports the interpretation made in Ch. 4 attributing this effect to the water H-bonding network stabilization/destabilization hypothesis. In accordance with this hypothesis, glucose with one more –OH group (i.e., 5 –OH groups) and larger dipole moment ($\mu = 3.8$) than fructose (4 –OH, $\mu = 3.2$) excludes a larger number of water molecules, making them unavailable to contribute to the overall energy absorption. Consequently, the ε' is decreased as the number of stronger water dipoles becomes limited in their reaction to the alternating EM field.

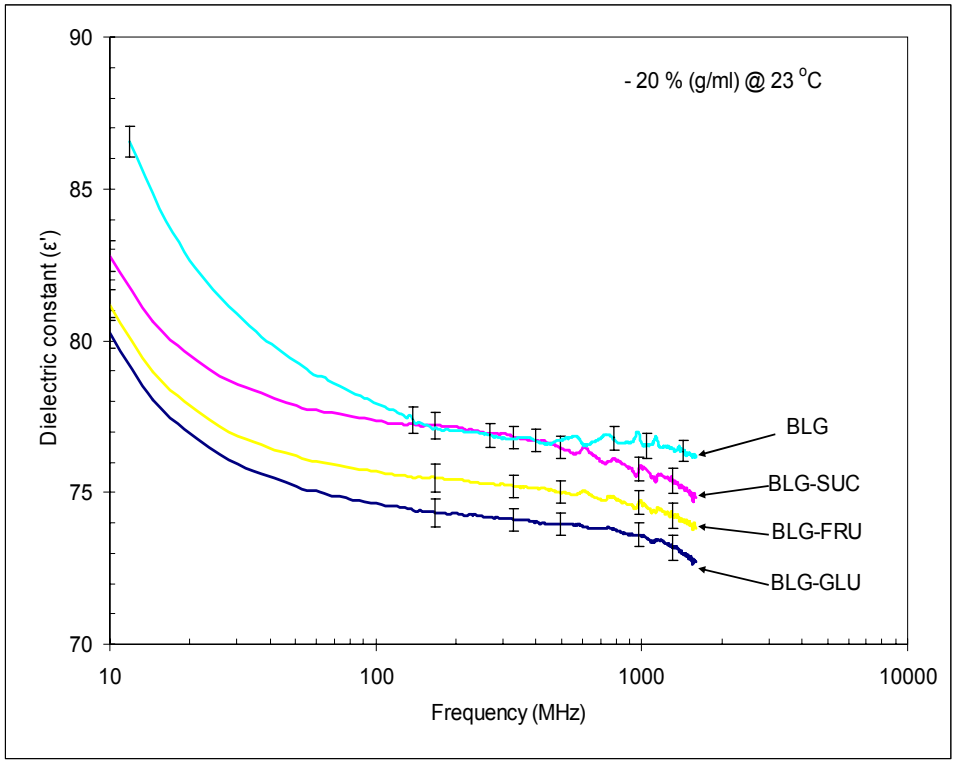

Figure 7.4.1.1. Dielectric constant spectra of protein-sugar (6:1) aqueous solutions [β-lactoglobulin sucrose (BLG-SUC), fructose (BLG-FRU), and glucose (BLG-GLU)] at 13% (wt/wt) concentration compared with a protein-only solution for the same amount of protein content. All measurements were made at 23°C.

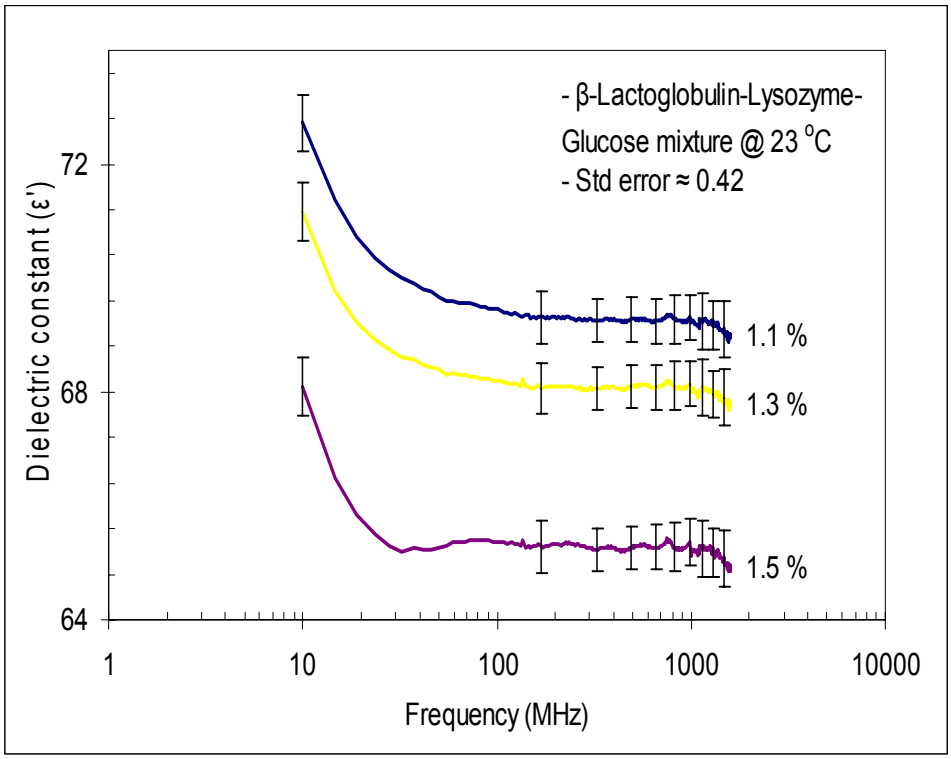

Figure 7.4.1.2. Dielectric constant (ε') response to EM field frequency variation for a β-lactoglobulin-glucose-lysozyme mixture. Glucose content was 0.33 g/ml throughout, while the lysozyme content was successively increased from 1.1% to 1.5%.

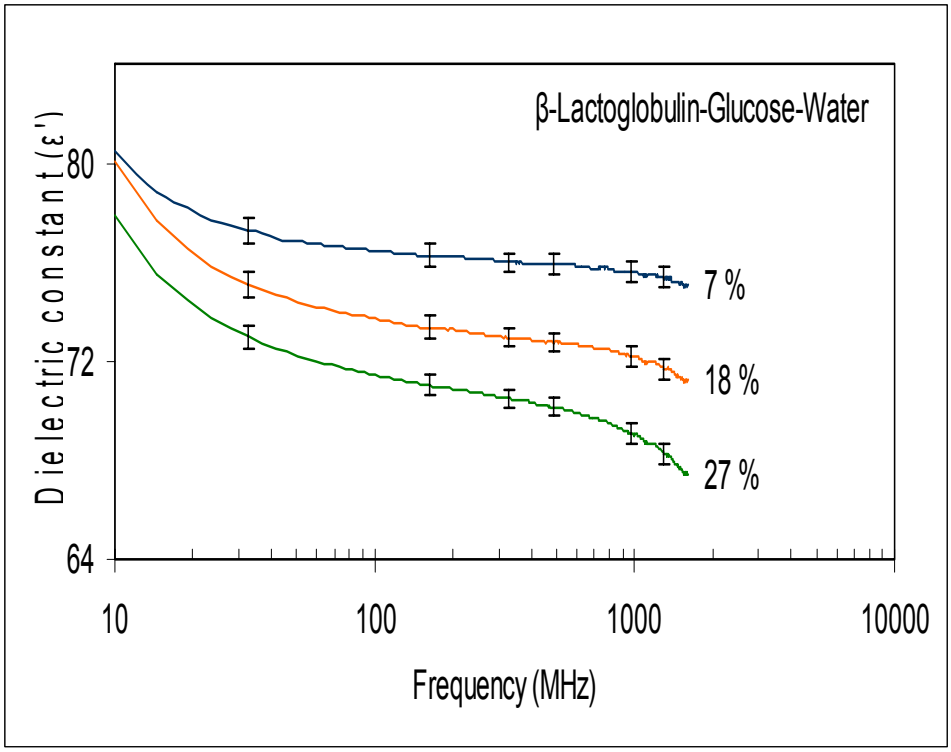

Figure 7.4.1.3. Dielectric constant (ε') as a function of field frequency for a β-lactoglobulin-glucose aqueous solution at 25°C.

Sucrose has almost twice the number of –OH groups (8 groups) than glucose and fructose and a much higher dipole moment (μ = 8.3), yet it registers a lower dielectric constant. This behavior can be attributed to its larger size, which slows it response to the alternating field and results in a lower depression of the solution's overall dielectric constant. The dynamics of the interactions between sucrose molecules and the EM field are still not well-defined, especially with temperature variations (see Ch. 3 for more details). Padua (1993) showed that after about 33% sucrose concentration, the dielectric behavior of the solution changes considerably. Another considerable change in the dielectric behavior of sucrose, in terms of relaxation rate, was observed by Padua and Schmidt (1992) and attributed to the formation of sucrose clusters beyond a certain

concentration that possibly become held by water bridges, resulting in slower reorientation with the alternating field and thus lowering the solution's dielectric constant.

The anomaly in the dielectric mechanism due to presence of sucrose molecules in mixtures can also be observed in Figs. 7.4.1.3, 7.4.1.4, and 7.4.1.5. Beyond certain concentrations (23% in this study), the dielectric behavior of solutions with sucrose appears to shift relative to those of glucose and fructose. This change becomes more pronounced as the field frequency increases, as can be seen when comparing results from the 27 MHz frequency with those from the 915 MHz and 1,800 MHz frequencies (Figs. 7.4.1.3, 7.4.1.4, and 7.4.1.5).

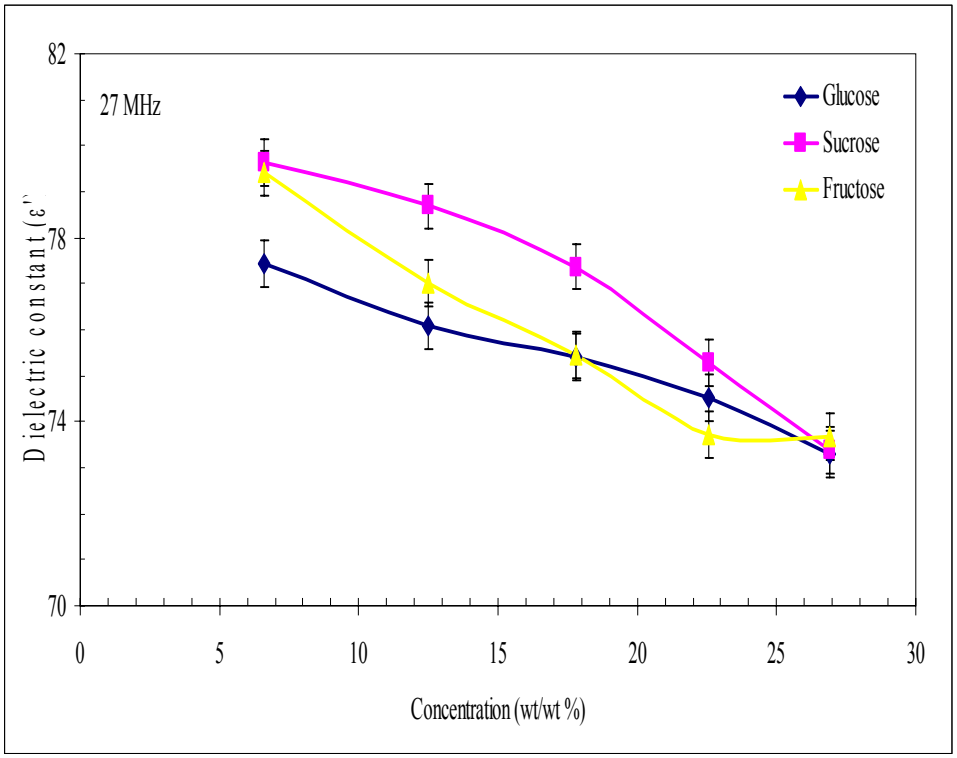

Figure 7.4.1.4. Dielectric constant as a function of complex concentration at 27 MHz for β-lactoglobulin-glucose, fructose, and sucrose solutions. The protein/sugar

ratio is held constant by successive dilution with deionized water. All measurements were made at 25°C.

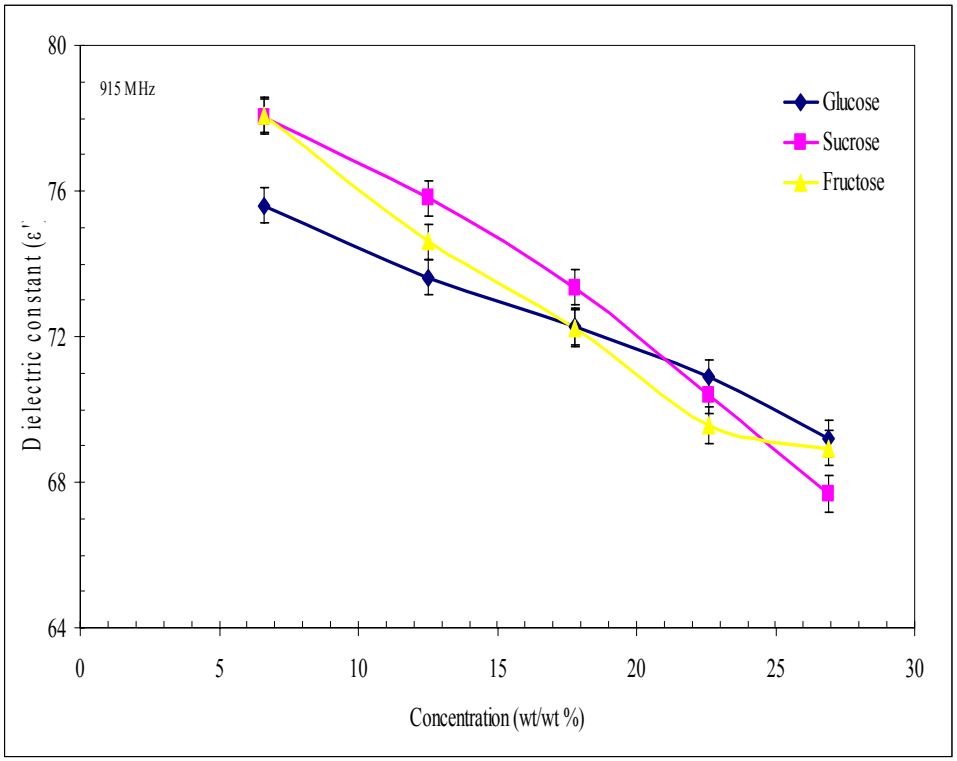

Figure 7.4.1.5. Dielectric constant as a function of complex concentration at 915 MHz for β-lactoglobulin-glucose, fructose, and sucrose solutions. The protein/sugar ratio is held constant by successive dilution with deionized water. All measurements were made at 25°C.

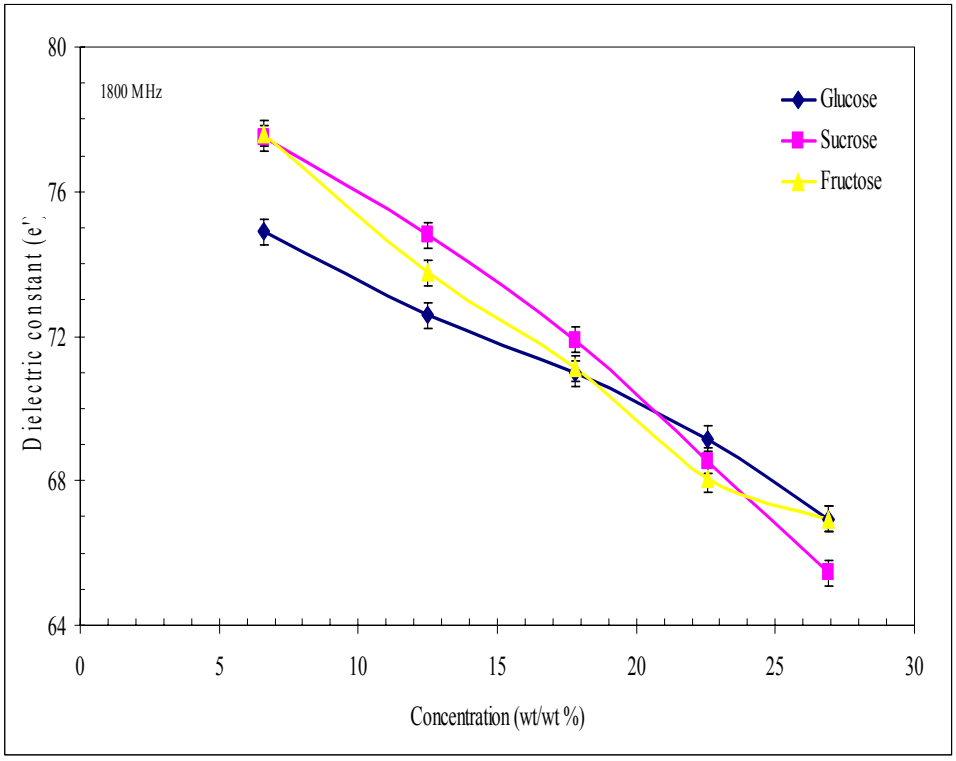

Figure 7.4.1.6. Dielectric constant as a function of complex concentration at 1,800 MHz for β-lactoglobulin-glucose, fructose, and sucrose solutions. The protein/sugar ratio is held constant by successive dilution with deionized water. All measurements were made at 25°C.

The calculation results from the mixture models used in this study (i.e., Rayleigh, Böttcher, and Berentsveig) for 27 MHz and 915 MHz are provided in Tables 7.4.1.1 and 7.4.1.2. Predicted values closely matched the experimental data from the three models for both frequencies, except for the β-lactoglobulin-glucose-lysozyme solution using the Rayleigh model. This was unexpected, and the only explanation that can be provided here is as follows: the Rayleigh model is a generalized formula that was derived by modifying the Maxwell model originally derived for the electrical conductivity of aqueous ionic solutions (Mudgett 1986). Thus, with the addition of lysozyme to the two-component mixture, the three contributions to the model are no longer comparable since the mixture

has become binary with interactive and non-interactive constituents. In other words, once a substance with much higher ionic strength (i.e., lysozyme) is introduced into a solution with other solutes that have a much lower ionic strength (sugars), the interactions of the ions with the applied field dominate, hence influencing the dielectric properties significantly. This effect is apparent in the experimental data for the three-component mixtures and calculated values in Tables 7.4.1.2 and 7.4.1.3.

Table 7.4.1.1. Measured vs. calculated dielectric constants for protein-sugar mixtures for 27 MHz frequency at 20% (wt/wt) concentrations and 20°C.

Mixture	$\varepsilon_{experiment}$	$\varepsilon_{calculated}$ (Rayligh)	$\varepsilon_{calculated}$ (Böttcher)	$\varepsilon_{calculated}$ (Berentsveig)
β-Lactoglobulin-Glucose-Lysozyme	65.30	37.52	75.63	75.02
β-Lactoglobulin-Glucose	75.42	69.39	71.95	71.43
β-Lactoglobulin-Sucrose	77.37	73.72	74.47	74.30
β-Lactoglobulin-Fructose	75.45	73.72	74.47	74.30

[a]The dielectric constants for the sugars were calculated using the Böttcher model for a two-component system, whereas for lysozyme the value was obtained from the molecular model discussed in Ch. 4.

Table 7.4.1.2. Measured vs. calculated dielectric constants for protein-sugar mixtures for 915 MHz frequency at 20% (wt/wt) concentrations and 20°C.

Mixture	$\varepsilon_{experiment}$	$\varepsilon_{calculated}$ (Rayligh)	$\varepsilon_{calculated}$ (Böttcher)	$\varepsilon_{calculated}$ (Berentsveig)
β-Lactoglobulin-Glucose-Lysozyme	65.26	37.33	75.07	74.41
β-Lactoglobulin-Glucose	72.27	68.03	71.08	70.48
β-Lactoglobulin-Sucrose	73.35	70.36	72.26	71.86
β-Lactoglobulin-Fructose	72.23	71.83	73.10	72.82

[a]The dielectric constants for the individual sugars were calculated using the Böttcher model for a two-component system, whereas for lysozyme the value was obtained from the molecular model discussed in Ch. 4.

7.4.2. Dielectric Loss

The general dielectric loss trend exhibited by the protein-sugar solution is shown in Fig. 7.4.2.1. A significant decline of the dielectric loss is evident at the lower frequency bands (i.e., f <200 MHz), followed by a leveling behavior in the intermediate bands (200–800 MHz), then a minor increase at higher frequencies (f >800 MHz) for all examined mixtures. Sucrose mixtures again deviated from the expected behavior, especially at the lower frequency range (i.e., 200 MHz). According to the dielectric loss interpretation based on the Brownian mechanism, larger molecules are expected to demonstrate lower reorientation rates with the alternating field, and thus higher energy loss. At higher frequencies, however, the molecular size-dielectric loss relationship seems to apply (see inset chart, Fig. 7.4.2.1). Sucrose solutions registered higher and progressively increasing dielectric loss compared to the smaller molecules. Again, this behavior may, to a great extent, be masked by the dielectric response of the water molecules.

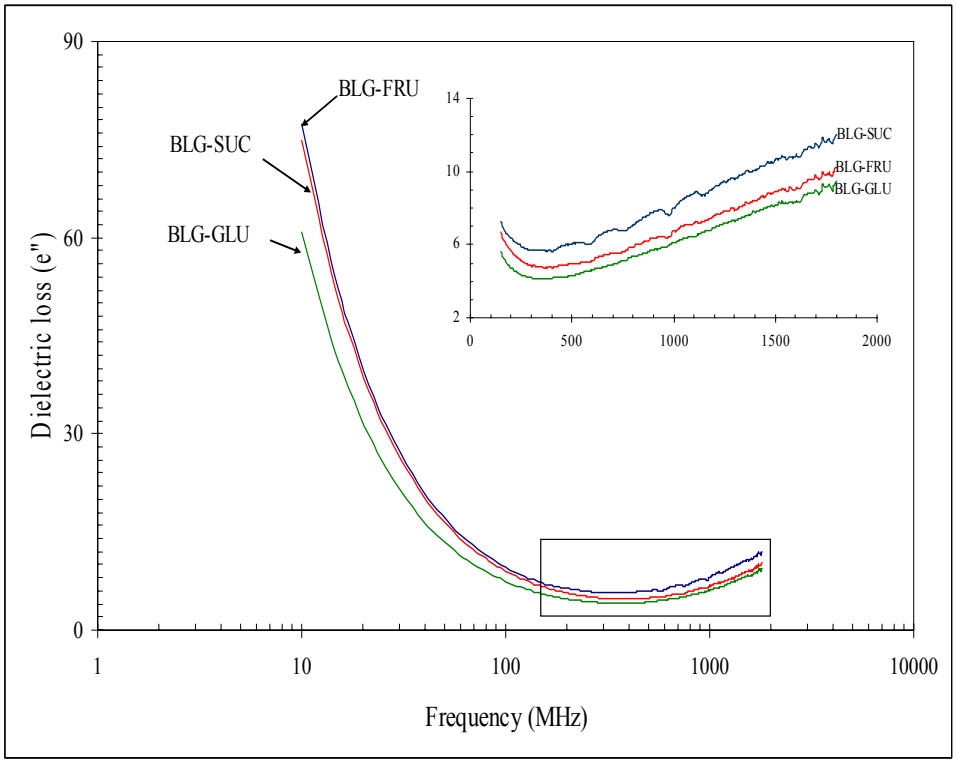

Figure 7.4.2.1. Dielectric loss factor for β-lactoglobulin-glucose, fructose, and sucrose solutions as a function of electrical field frequency at 18% (wt/wt) concentrations and 23^{o}C.

The concentration influence on the dielectric loss of the protein-sugar mixture was typical for all examined solutions; representative data is shown in Fig. 7.4.2.2. Increasing the solutes' content (while maintaining a fixed ratio) resulted in depressing the dielectric loss considerably at lower frequencies, but only slightly at higher frequencies (Figs. 7.4.2.2 and 7.4.2.3). This behavior agrees with the interpretations that attribute the higher loss at lower frequencies to resistive heating losses primarily caused by molecular and ionic migration between the material's boundaries (Hagmann et al. 1992, Piyasena et al. 2003). At higher frequencies, conductive losses diminish, and dipolar rotation becomes the dominant contributing mechanism to the overall loss.

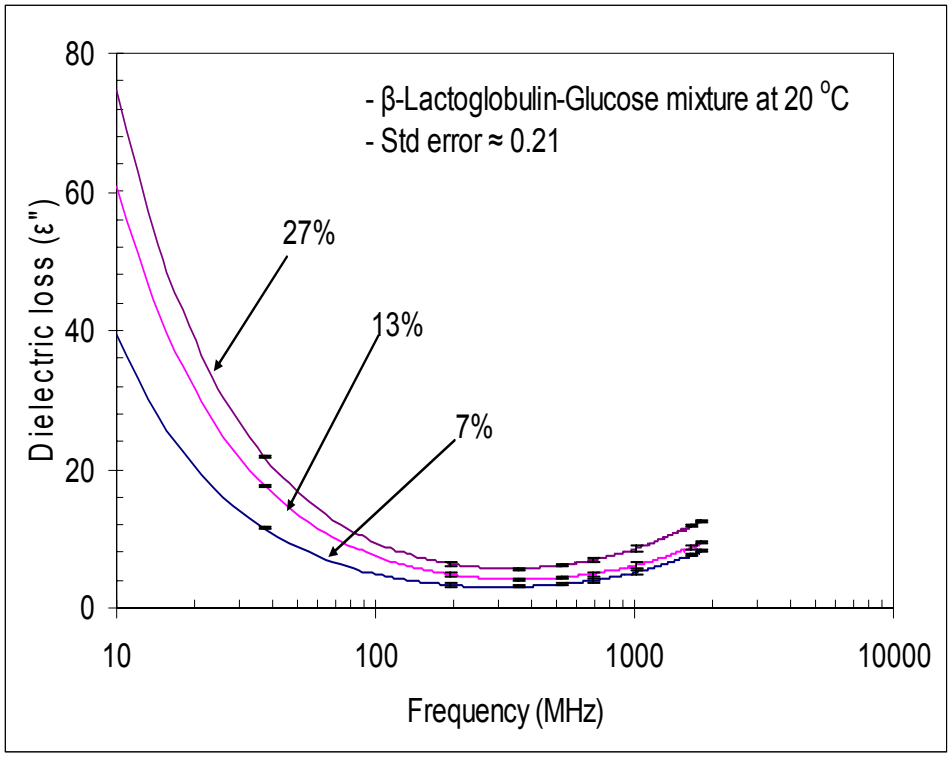

Figure 7.4.2.2. Dielectric loss (ε") response to frequency variation for β-lactoglobulin-glucose aqueous solution at 20°C. The inset shows the tendency of an infliction point at a specific frequency (between 300 and 400 MHz).

Introducing lysozyme to the β-lactoglobulin-glucose mixture resulted in shifting the overall dielectric behavior of the solution at higher frequencies (>1,000 MHz), as shown in Fig. 7.4.2.3. Lysozyme, with much more ionic strength than the other components in the mixture, lowered the overall loss of the mixture at higher frequencies and resulted in an infliction point at frequencies close to 900 MHz. At this frequency band, the dielectric loss shift was dipolar-dominant, causing contributions due to lysozyme content to shift from being higher for higher concentrations at the lower frequencies to being lower at higher frequencies (Fig. 7.4.2.3).

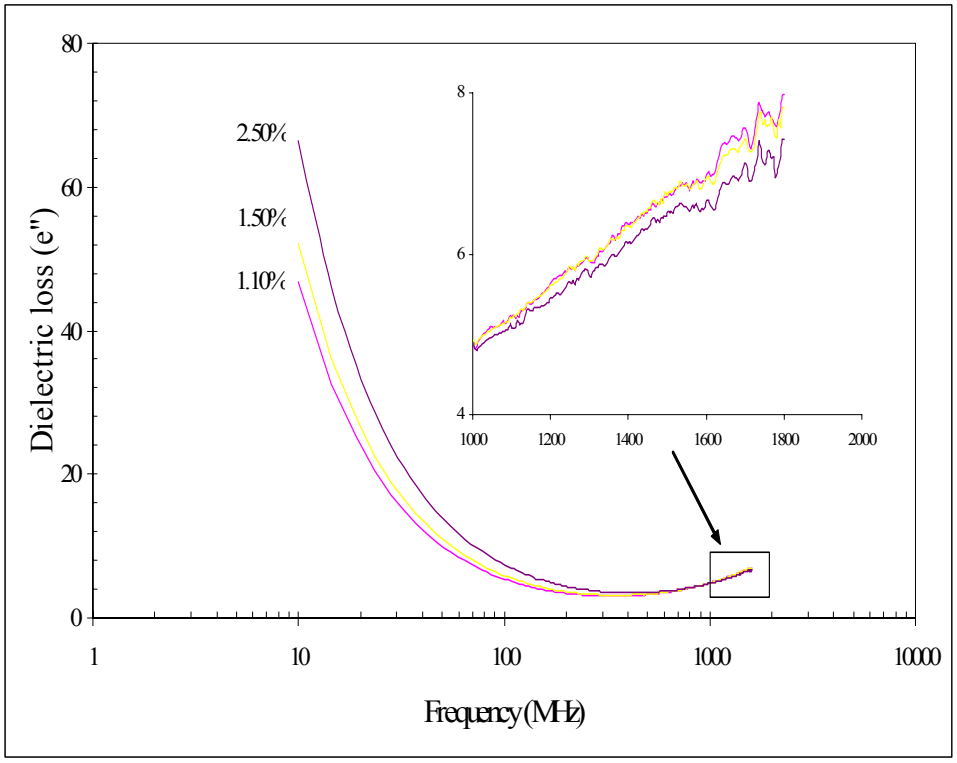

Figure 7.4.2.3. Dielectric loss (ε") response to frequency variation for β-lactoglobulin-glucose-lysozyme aqueous solution at 23°C. The inset shows the tendency of an infliction point at a specific frequency (between 300 and 400 MHz).

7.5. SUMMARY AND CONCLUSIONS

The goal of finding a model capable of predicting the dielectric properties of foods for dielectric heating purposes may be reached if a systematic and practical approach is followed when studying the dielectric behavior of food materials. In this study, an integration approach was followed by first examining the dielectric behavior of food constituents individually and in combination in an aqueous environment. The primary objective of this study was to quantitatively determine the contributions of food carbohydrates and proteins to the mixture's overall dielectric properties at selected

frequencies (27 MHz and 915 MHz) relevant to industrial dielectric processing of foods. Once individual contributions are computed, known mixture models can then be utilized to predict the overall properties of the mixture.

In this work, three mixture models (Rayleigh, Böttcher, and Berentsveig) commonly used for moist media were utilized to calculate the mixtures' dielectric constants. Results were compared to the experimental data and agreed fairly well, except for those obtained from the Rayleigh model. These model results underestimated the experimental value by almost one half, for which causes were attributed to the dominating effect of the lysozyme contribution. The dielectric constant for lysoyme used in the model was a theoretical value calculated from its amino acid composition in a static field. This value (2.7) was much lower than the values used for the sugars, which ranged from 38 to 49. This substantial difference influenced the calculated value considerably.

The influences of concentration, molecular size, and frequency on the mixtures' overall dielectric properties were also examined. Solute concentration caused a depression in the dielectric constant and loss factor, with much larger magnitudes at lower frequencies. At higher frequencies, the decrements of both properties, constant and loss, were minimal and causes were attributed to the nature of the dielectric mechanism at the frequency range of concern. These mechanisms were also related to the response of the dielectric properties to the field's frequency variations. The examined frequency range (10–1,800 MHz) was divided into three distinct regions with respect to the dielectric behavior of the mixtures. The dielectric behavior at the lower frequency range

was attributed to the ionic conduction mechanism, and the upper region to the dipolar mechanism. The intermediate region was not investigated.

7.6. REFERENCES

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CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

Dielectric properties of biological materials are of major interest to scientists and engineers involved in the field of dielectric heating and thermal processing. The ability to predict and quantify these parameters and their responses to a variety of physical, chemical, and electrical changes is essential for every designer and researcher alike. Unit operations equipment, industrial processing line optimization, and numerical simulations analysis are among the many tasks that depend upon correct and reliable prediction models of dielectric properties. The potential advantages of electromagnetic (EM) heating methods for reduced processing times, uniform product heating, and improved product quality in selected applications are well established. However, the potential economic advantages are still to be realized and their dependence on a knowledgeable evaluation of product chemical composition, physical state, and heating characteristics still needs to be explored.

This work aimed at extending prior efforts of characterizing and predicting the dielectric behavior of biological material to multi-component systems to add to the existing prediction models (i.e., contribute to their modifications for broader applications. The approach taken was both theoretical and experimental. Theoretical investigations were conducted via evaluating existing quantitative prediction models for foods and their biochemical constituents, individually and in mixtures. Experiments were conducted by measuring the dielectric properties of representative food constituents' solutions under various physical and chemical conditions.

The dielectric mechanism of food carbohydrate solutions (starch, sucrose, glucose, and fructose) was characterized over the frequency range 10–1800 MHz at 20–100^{o}C. The influences of field frequency (*f*), temperature (T), and concentration (C) on the dielectric constant (ε') and loss factor (ε") were examined and theoretically interpreted. Results from food protein investigations showed that the dielectric mechanisms exhibited by all examined proteins were typical of protein solutions for the selected concentration levels (i.e., agreed with previously published studies). The α and γ-dispersions were clearly observed for all proteins for which the last segment of the α-dispersion curve was evident in the 5–10 MHz interval of the spectrum; the initial stage of the γ-dispersion was observed at frequencies beyond 1 GHz. Ionic release from proteins was evident from both the behavior of ε" and electrical conductivity, which continuously increased with increasing protein content. Previously reported sub-dispersions (δs) between β and γ-dispersions for protein solutions were observed, albeit at higher relaxation frequencies than those reported in prior investigations. Clearly separated delta-dispersions were observed at 550 MHz, 750 MHz, and 970 MHz. These δ-dispersions were proposed as being a sub-unit of multiple dispersions that exist between the β and γ-dispersions.

Protein dielectric contributions were computed from the amino acid sequence using computed average molecular polarization and Mw. Results showed that proteins in solutions on average absorbed about 3.5–10% of the applied energy. Computation of ε' for the six selected proteins resulted in values between 2.66 and 2.72. The derived mixture equation appeared to provide a prediction capability of the dielectric constant (ε'), and consequently ε" via the Kramers-Kronig relations, at frequencies close to 915

MHz. For three and four-component mixtures, mathematical models (i.e., Rayleigh, Böttcher, and Berentsveig) commonly used for most media were utilized to calculate the mixtures' dielectric constants. Results were compared to the experimental data and agreed fairly well.

The following may prove helpful in future studies:

1) Spectroscopic characterization of dielectric materials and their composition necessitate the use of a much wider frequency range (e.g., KHz to GHz). Selecting a narrow frequency band increases the risk of missing the relaxation range of interest. Also, mixtures comprising molecules differ in their relaxation rates, with some relaxing at much lower or higher frequencies than others.

2) For foods, it would be beneficial to first start investigating the sate of the water (i.e., free or bound) and its binding structure. Quantifying the free water content and isolating its contribution to the overall mechanism should simplify the task of accounting for the contributions from rotational-bound water molecules.

3) It is highly recommended to extend the experimental procedure to include runs with a MW or RF oven in order to assess the impact of the variations of the dielectric properties on the overall energy absorption and conversion.

4) Simulation studies are also recommended to assess the prediction capability of the selected mixture models.

5) Due to their high sensitivity, dielectric measurement devices can be unreliable, and comparison of results from one setup to another may prove helpful when drawing conclusions.