

DIELECTRIC PROPERTIES AND THEIR APPLICATION IN MICROWAVE-ASSISTED ORGANIC CHEMICAL REACTIONS

by

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A thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfillment of the requirements for
the degree of Doctor of Philosophy

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0-612-78716-8

Suggested Short Title:

Dielectric Properties and their Application in Chemical Reactions

ABSTRACT

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This study was designed to develop some predictive models for the dielectric properties of the chemicals and chemical reactions and make use of dielectric properties and microwave irradiation in the chemical reactions. Specifically, the dielectric properties of the following systems were investigated at microwave frequencies of 2450 and 915 MHz: (1) C₁-C₅ alcohols; (2) glucose aqueous solutions, (3) lysine aqueous solutions, (4) mimicked esterification reaction model systems of parahydroxybenzoic acid with methanol, 1-propanol and 1-butanol in the presence of para-toluene sulfonic acid as a catalyst, (5) Maillard reaction model system consisting of glucose, lysine and water.

The dielectric properties of the model systems showed that they depended on the frequency applied, concentration of the material, and temperature. Most of the predictive models showed that there exists a linear or quadratic relationship between dielectric constant and concentration or temperature. However, the quadratic equation is better than the linear one to describe the variation of the loss factor with temperature or concentration.

Esterification showed great advantages for the use of microwave irradiation in chemical reaction. It included reduction in reaction time, and provided distinct temperature profiles due to microwave environment during chemical reactions. The reason for rate enhancement of this type of reaction was also demonstrated from the temperature profile.

Microwave-assisted solvent free Maillard reaction model system, consisting of glucose and lysine, demonstrated that the heating method applied was not one of the crucial factors, but the temperature level was important during the chemical reaction.

The relationship of loss factor with yield of reaction showed that it is possible to use dielectric data to analyze, and monitor the chemical reaction. It provided a new methodology to analyze the reaction.

The relationship between the loss factor, loss tangent and the reaction time, and concentration of the material showed that it is also possible to use dielectric data at microwave frequencies of 2450 and 915 MHz to study chemical reactions, especially the kinetics.

Les propriétés diélectriques et leur application dans les réactions chimiques organiques assistées par micro-ondes

RÉSUMÉ

Cette étude fut établie afin d'élaborer des modèles de prévision des propriétés diélectriques de produits lors de réactions chimiques pouvant tirer profit de ces propriétés diélectriques et de l'énergie micro-onde. Les propriétés diélectriques des systèmes suivants ont été étudiées aux fréquences micro-ondes de 2450 et 915 MHz: (1) alcools C₁-C₅; (2) solutions aqueuses de glucose; (3) solutions aqueuses de lysine; (4) mimétisme de modèles d'estérification d'acide parahydroxybenzoïque avec méthanol, 1-propanol et 1-butanol en présence d'acide sulfonique para-toluène à titre de catalyseur; (5) modèles de réaction de Maillard composés de glucose, lysine et eau.

Les propriétés diélectriques des préparations modèles ont démontré dépendre de la fréquence micro-onde employée, de la concentration du matériau, et de la température. La plupart des modèles prédictifs ont démontré qu'il existe une relation linéaire ou quadratique entre la constante diélectrique et la concentration ou la température. Cependant, une relation quadratique s'est avérée mieux décrire la variation du facteur de pertes en fonction de la température ou de la concentration.

L'estérification a démontré le grand avantage de l'utilisation de l'énergie micro-onde lors des réaction chimiques, avec une réduction du temps de réaction, permettant une courbe de température distincte causée par l'environnement micro-onde lors de la réaction chimique.

La modélisation de la réaction de Maillard sous environnement micro-onde sans solvant, composée de glucose et de lysine, a démontré que le procédé de chauffage n'est pas l'élément critique, mais plutôt la température atteinte lors de la réaction chimique.

La relation du facteur de pertes avec le rendement de la réaction a démontré qu'il est possible d'utiliser les valeurs des propriétés diélectriques dans l'analyse et le contrôle des réactions chimiques, offrant ainsi une nouvelle approche analytique des réactions.

La relation entre le facteur de pertes, le facteur de dissipation et le temps de réaction, et la concentration du matériau, a démontré qu'il est possible d'utiliser les valeurs des propriétés diélectriques aux fréquences de 915 et 2450 MHz, lors de l'étude de la cinétique des réactions chimiques.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deep sense of gratitude and sincerest thanks to my thesis supervisor, professor Vijaya Raghavan, Department of Agricultural & Biosystems Engineering, Macdonald Campus of McGill University, for his valuable guidance, critical suggestions, encouragement and help in the completion of present work. I also wish to convey my sincerest thanks to co-supervisor, Dr. Varoujan A. Yaylayan, Department of Food Science & Agricultural Chemistry, Macdonald Campus of McGill University, for his constructive criticism, encouragement and many helpful suggestions throughout this work. I would also like to thank professor Zhun Liu, The Research Institute of Elemento-Organic Chemistry, NanKai University, P. R. China, for his encouragement and selecting me to participate this great and wonderful project.

I would like to thank Dr. Akyel and Mr. Jules Gauthier for their generosity in providing equipment for some parts of the experiments in the thesis carried out at Ecole Polytechnique.

Special thanks are extended to the distinguished members of my comprehensive examination committee: Dr. Vijaya Raghavan, Dr. Varoujan A. Yaylayan, Dr. Suzelle Barrington, Dr. Arun S. Mujumdar, Dr. J. R. Jocelyn Paré for their critical review and constructive comments on my research proposal of Ph. D thesis.

I thankfully acknowledge the generous help and cooperation of my friends and colleagues in the department. The help from Dr. Valérie Orsat, Venkatesh Meda, Jianming Dai, Guiping Wu, Tim Rennie, Venkatesh Sosle, Essau Sanga, Dr. Sam Sotocinal, Zhanhong Liu is truthfully acknowledged.

I am grateful for the financial support from CIDA (Canadian International Development Agency) throughout this work. Also financial assistance of NSERC is greatly appreciated.

I sincerely express my appreciation to my big family, especially to my beloved parents, parents in-law for their love and support. The sincerest appreciation is given to my dear wife, Hong Ma, for her love, moral support, and constant encouragement.

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NOMENCLATURE

α	a constant indicating the measure of the interaction
ε	complex permittivity
ε_m	permittivity of the mixture
ε^*	complex permittivity of the material
ε'	dielectric constant of the material
ε''	loss factor of the material
ε_w'	dielectric constant of pure water
ε_w''	loss factor of pure water
ε_s'	dielectric constant of an aqueous ionic solution
ε_s''	loss factor of an aqueous ionic solution
ε_s	static dielectric constant
ε_o	optical dielectric constant
λ	wavelength
λ_0	wavelength in free space
λ_s	critical wavelength
μ	complex magnetic permeability
v	volume fraction
ρ	material density, g/cc
ω	complex resonant angular frequency
c_p	specific heat, J/g°C
Λ	equivalent conductivity of the solution
C	dissolved salts concentration
E	microwave electric field
H	microwave magnetic field
L	energy loss per cycle

P	power absorbed in watts/m ³
V _c	region enclosed by the cavity
Γ	band-width at half-maximum.
<W>	time-averaged energy stored in the cavity
CA	chemical abstract
MW	microwave
CIE	commission internationale d'éclairage
CDA	color dilution analysis methods
DMF	dimethyl formamide
PTSA	toluenesulfonic acid
HDTMAB	hexadecyltrimethylammonium bromide

I. GENERAL INTRODUCTION AND OBJECTIVES

1.1 Introduction

Microwave is used as one of the energy forms to drive the chemical reaction. Microwave heating is much distinctive from the conventional heating methods such as conduction, convection and radiation. Dielectric properties of materials are key parameters in the application of microwaves as a new technology for organic synthesis and extraction of active ingredients because the temperature profile during microwave process is directly associated with them. Data on dielectric properties of many food materials, some chemicals, especially the common solvents such as petroleum ether, ethyl acetate, lower carbon alcohol, acetone and DMF (dimethyl formamide) can be obtained from the literature (Tinga and Nelson, 1973; Douglas and Marcel, 1987). The kinetic relationships between the dielectric constant, the reaction rate and the yield of the reaction were qualitatively reported by some researchers (Li et al., 1996, 1997; Zhang et al., 1997). However, these dielectric properties mentioned in the literature were not measured at the two commonly used microwave frequencies of 2450 and 915 MHz and the relationships between dielectric properties of chemicals, concentration, temperature, reaction rate and the yield of the reaction have not been studied extensively.

Microwave-heating rate has a strong functional relationship to the dielectric properties and electric field strength. For a given microwave instrument, it is not easy to change the microwave frequency and electric field strength. Therefore, in order to approach the optimum microwave heating, one of the ways is to change the dielectric properties of the materials through concentration changes. It is necessary to know the relationship of the dielectric properties and component (concentration) of the materials. The dielectric properties are also dependent on the temperature of the material. So it is also important to know the temperature profile of the components, in particular, when the reaction begins and approaches equilibrium. Recently, some researchers have reported the temperature profile of some digestions and some lower carbon alcohols using microwave heating (Kingston and Stephen, 1997; Palacios et al., 1996). The information about temperature profile during microwave heating can be useful in the following aspects:

- (1) To perform synthesis under microwave irradiation at known optimal conditions.

- (2) To correlate the behaviour of the materials with their physical and chemical properties.
- (3) To provide some insight for the mechanism of the microwave-enhanced chemical reactions, which will be helpful to design microwave reaction apparatus.

Since the appearance of the first papers on the application of microwave for organic synthesis (Gedye et al., 1986; Giguere et al., 1986), numerous papers regarding the application of this special technology in this field have been published (Kappe, 2001). Most microwave-assisted chemical reactions have been centred on the rate-enhancement of the reaction, timesaving, higher yields compared to the conventional heating methods such as oil bath, heat-mantle and electric oven. As for as the reasons for microwave-enhanced chemical reactions, only a few reports have questioned whether there exists any specific "microwave effects" on chemical reactivity owing to changes induced at the molecular level resulting from the absorption of microwave energy (Hajek, 1997). In addition, some basic theories about this interesting field have been discussed in the recent investigations (Westaway and Gedye, 1995; Stuerge and Gaillard, 1996; Li et al., 1997; Gedye and Wei, 1998; Mijovic et al., 1998; Adolf, 2001; Loupy et al., 2001). Among these, questions concerning temperature stability and uniformity of heating by microwaves have cast some roles on the interpretation of these results. The majority of claims for specific microwave acceleration have contributed to the special microwave temperature profile resulting in superheated solvents (Saillard and Berlan, 1995). However, Li et al. (1996) suggested that a specific effect may result purely from the faster increased heating rate which microwave dielectric heating offered other than the way obtained by conventional heating modes. In order to explain the microwave-assisted chemical reaction, it is important to know the temperature profile during the microwave irradiation. The activation of the molecule is strongly related to the temperature of the reactants. The reaction can happen only when the reactants are activated and give rise to the desired products.

The esterification of the p-hydroxybenzoic acid with lower carbon alcohols has been reported that it was greatly accelerated by microwave irradiation at a microwave frequency of 2450 MHz (Chen et al., 1993; Zhang et al., 1998). Lysine is an essential amino acid and it is most often the limiting amino acid in cereal products (Jokinen et al.,

1976). In order to achieve the objective of relationship between the chemicals, chemical reaction and dielectric properties, two types of the chemical reactions were chosen as models for the current investigation. They are esterification of p-hydroxybenzoic acid with lower carbon alcohols and Maillard reaction of glucose with lysine in water.

1.2 Objectives

The main objective of this study was to study the chemicals and chemical reaction from the aspect of dielectric properties at microwave frequencies of 2450 and 915 MHz (physical properties) not limited from the chemistry aspect. In pursuit of this main goal, the specific objectives of the study were:

- i) To establish relationships between dielectric properties of the chemicals and concentration through the measurement of dielectric properties.
- ii) To establish relationships between dielectric properties of the chemicals and temperatures.
- iii) To develop predictive models linking the dielectric properties of the chemical reaction to the yield of the reaction.
- iv) To develop methods using dielectric property analysis for trailing the two chosen chemical reactions in this study.
- v) To establish optimum condition for esterification under microwave environment.
- vi) To explain the mechanism of the microwave-assisted chemical reaction through yield comparisons of the reaction under microwaves and conventional heating at varying temperature profiles.

II. GENERAL LITERATURE REVIEW

The purpose of this review is to provide a perspective on the present state of the measurement methods, dielectric properties of the chemicals, dielectric properties of chemical reaction, microwave-assisted organic synthesis, application of dielectric properties, areas of development and debates yet to be resolved. A background about microwave and dielectric properties is also provided and literature about the mathematical models describing the dielectric properties of food material and their components is reviewed.

2.1 Dielectric Properties and Microwave Heating

2.1.1 Introduction to microwave

Microwaves are short wavelength electromagnetic waves generated by magnetrons and klystrons, consisting of electrical and magnetic energy. Microwaves lie between the radio frequencies and radar bands (Figure 2.1) (Kingston and Stephen, 1997). The wavelength ranges from 0.1mm to 1m (300 MHz to 300 GHz).

Microwaves have the same behaviour as the light-waves. They can be reflected by metal, transmitted by materials such as tetrachloromethane, benzene, alkane, glass, ceramics, plastic, paper which have lower dielectric properties; absorbed by such materials as water, lower carbon alcohol, dimethyl formamide (DMF) which have higher dielectric properties.

2.1.2 Dielectric properties

The dielectric properties of materials are key factors to be considered in microwave-assisted chemical reactions, because they are directly linked to the heat distribution of the materials during the microwave heating process. In fact, in a chemical reaction, it involves various parameters such as material variety, concentration of the material and temperature. The dielectric properties of a material can be expressed by the following equations:

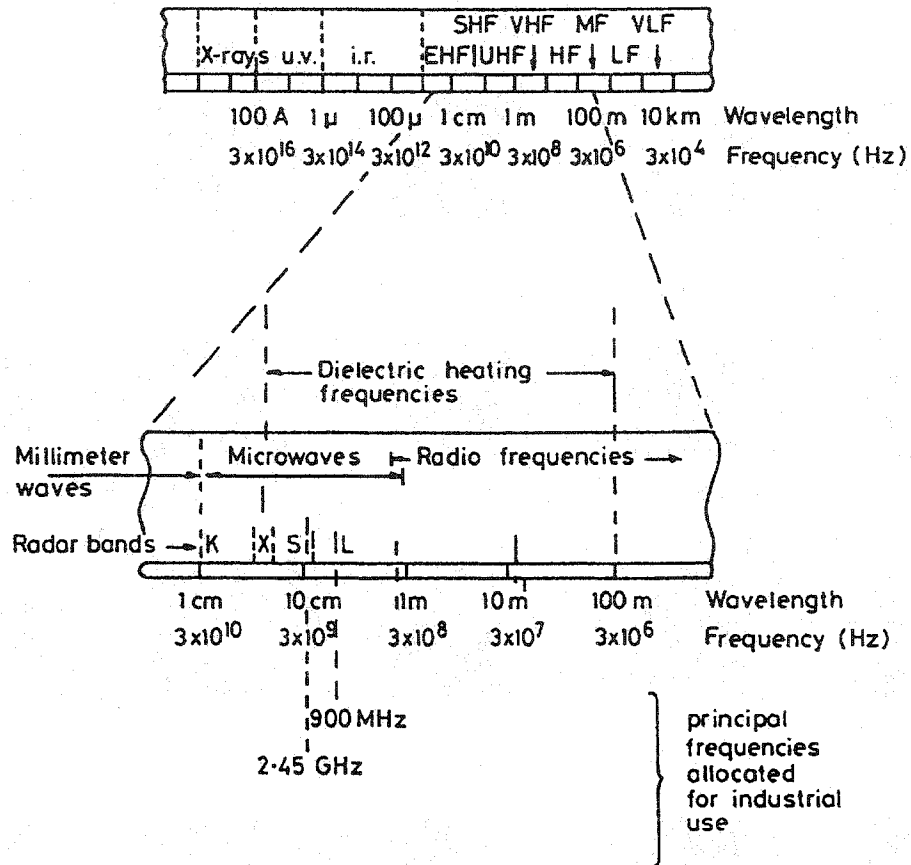


Figure 2.1: The electromagnetic spectrum.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2.1)$$

Where,

ϵ^* is the complex permittivity of the material. It contains two parts, a real part ϵ' and an imaginary part ϵ'' . It is related to its ability to couple electrical energy from a microwave power generator, e.g., a magnetron or klystron in terms of loading effects generally reflected by characteristic product impedance.

ϵ' is the dielectric constant of the material, which is a measure of the ability of a material to couple with microwave energy.

ϵ'' is the dielectric loss factor of the material, which is a measure of the ability of a material to dissipate electric energy, converting it into heat.

In addition, the ratio ϵ''/ϵ' is called the loss tangent ($\tan\delta$), which is related to the ability of materials to be penetrated by an electrical field and to dissipate (attenuate) electrical energy as heat. Generally, the higher the value of the loss tangent is, the better the material will absorb microwave energy. These dielectric properties are considerably dependent on such factors as frequency, the concentration of the chemical reactants, and the initial temperature of the compounds. The dielectric properties of most food materials have been reviewed by Tinga and Nelson (1973) and some chemicals at 2450 MHz have also been reviewed by Gabriel et al. (1998).

2.1.3 Microwave heating

Microwave heating is a volumetric process, which is distinctive from other conventional heating mechanisms. The volumetric heat results in temperature increase in the interior of the material. The theory of microwave heating has been extensively discussed in the literature (Whittaker and Mingos, 1994). There are two mechanisms about microwave heating: dipole rotation and ion polarization (Decareau and Peterson, 1986). The former occurs when polar molecules such as water, dimethyl formamide (DMF) and lower carbon alcohol are exposed to electromagnetic field. The materials will be heated and the weak hydrogen bonds will be disrupted as a result of the molecules friction. In contrast, the latter occurs in samples containing ions such as electrolytes. In the presence of an electromagnetic field, the positive ions (e.g., K^+ that exists in the chemical reaction by phase transfer catalysis) perform electrophoretic migration toward to the negative pole. They collide with other ions and molecules so that the heat is generated. When dielectric loss occurs, the absorbed microwave power energy can be dissipated as heat. The amount of power absorbed and the rate of heat generation depend upon the dielectric properties of the materials, the intensity and frequency of the field. The relationships can be expressed by the following equations [Goldblith, 1967]:

$$P = 55.61 \times 10^{-12} f \epsilon'' E^2 \quad (2.2)$$

$$\frac{dT}{dt^*} = \frac{55.63 \times 10^{-12} f \epsilon'' E^2}{\rho c_p} \quad (2.3)$$

Where,

P = power absorbed in W/m³.

E = voltage gradient in volts/m.

T = temperature of the materials, °C.

f = frequency of the energy source in 1/s.

ρ = material density, g/cc.

ε'' = dielectric loss factor of the material.

t* = time, s.

c_p = specific heat, J/g°C.

Microwave heating is not only relevant to the dielectric properties of materials, but also to electric transmission properties (Decareau, 1985). In some sense, the microwave dielectric heating effect takes advantage of the ability of some chemicals to transform electromagnetic energy into heat and thereby drive chemical reactions.

The properties of the equipment and the materials being heated have crucial influences on the heating of materials by microwaves (Schiffmann, 1986). The frequency and power of the microwaves are important parameters of the microwave system, which contribute to the microwave heating. The impact of each of these must be considered in the design of a product/processing system. Any dipolar compound with relatively low molecular weight will tend to display a capacity for heat in the presence of microwave field. The temperature rise profiles for some chemicals under microwave irradiation are shown in Tables 2.1 and 2.2.

*Table 2.1: Heating of organic solvents by microwaves (50cm³, 560 Watt for 1 minute)
(Whittaker and Mingos, 1994).*

Compound	Temp.* (°C)	B. P.** (°C)	Compound	Temp.* (°C)	B. P.** (°C)
Water	81	100	Acetic acid	110	119
Methanol	65	65	Ethyl acetate	73	77
Ethanol	78	78	Chloroform	49	61
1-Propanol	97	97	Acetone	56	56
1-Butanol	109	117	DMF	131	153
1-Pentanol	106	137	Diethyl ether	32	35
1-Hexanol	92	158	Hexane	25	68
1-Chlorobutane	76	78	Heptane	26	98
1-Bromobutane	95	101	CCl ₄	28	77

*: Temp: Temperature; **: B.P.: Boiling point.

2.1.3.1 Frequency

Microwave frequencies of 915 and 2450 MHz are often used in industries and research labs. Their wavelengths in air are 33 and 12.2 cm, respectively. From the microwave power Equation (2. 2), we can see that higher the microwave frequency used in the microwave field, more the energy can be available for the material. However, for a given microwave system, due to the fact that the microwave frequency is not adjustable, the better way to afford better microwave heating efficiency is to modify the other parameters affecting the microwave heating.

Table 2.2: Comparison of heating effect (50cm³ Microwave at 2450 MHz irradiation for 15 s at 525W) (Zhang et al., 1997).

Solvent	Temperature after microwave irradiation (°C)	Boiling point (°C)	Static dielectric constant (ϵ_s)
1-Propanol	60	97	20.1
1-Butanol	53	117	17.8
1-Pentanol	48	137	13.9
1-Hexanol	41	158	13.3
CHCl ₃	21	62	4.8
Acetic acid	35	118	6.2
1-Butanone	39	80	18.5

2.1.3.2 Thermal properties

The thermal properties of chemicals being heated include the heat capacity and thermal conductivity, which have an important influence on the product (Equation 2.3). As the heat capacities increase, the heating rates decrease in a smooth way (Figure 2.2).

2.1.3.3 Temperature

Heating rate not only depends on the power level but also on the initial temperature of material due to the fact that the dielectric properties vary with temperature. The dielectric loss may increase or decrease with temperature, depending on the intrinsic properties of the material being heated. Since the temperature changes during microwave heating, it may have a profound effect on the dielectric constant, dielectric loss factor, and it is important to know what functional relationships exist between these parameters in

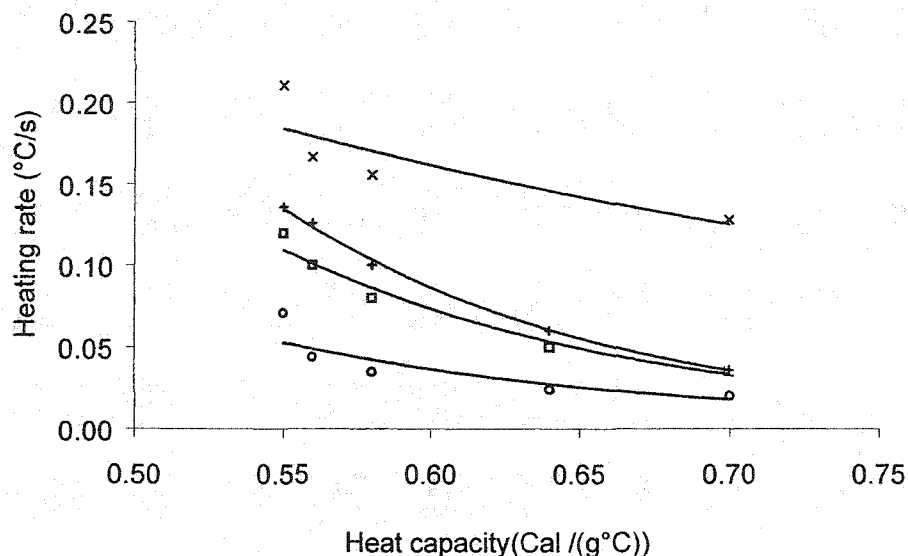


Figure 2.2: The heating rate plotted against heat capacity for (o) water, (□) ethanol, (+) butanol and (x) hexanol at a power of 233W in the temperature range of 20-60 °C (Palacios et al., 1996).

any material. However, it is not easy to get the measurements of time-temperature profiles within a product during microwave heating using conventional temperature sensors (i.e. thermometers, thermocouples). Those conventional sensors interact with the magnetic component of the field and may also cause arcing at sensor surface and result in flame and explosion during the chemical reaction. While the temperature profiles can be measured by glass thermometers containing fluid with low thermal expansion coefficients, less efficient to absorb microwaves or by developed fibre optic methods that are not significantly affected by the microwave field. The disadvantage for these two methods mentioned is that these measurements are expensive. Accordingly, time-temperature profiles are generally measured by conventional sensors following irradiation for discrete time periods by inserting temperature probes at various positions within the reaction.

2.1.3.4 Microwave heating rate

The heating rate of materials by microwaves is affected by a number of properties of the equipment and the materials being heated. These properties include the dielectric constant, loss factor, specific heat capacity, emissivity of the sample and the strength of the applied field and temperature. Palacios et al. (1996) have done some research about the microwave heating profiles and property-structure relationships in a family of alcohols. They found that the normal-alcohols from C_1 to C_6 have higher heating rates than pure water. This result can be useful when selecting a heating media for chemical reaction or extraction under microwave irradiation (Figures 2.3 and 2.4).

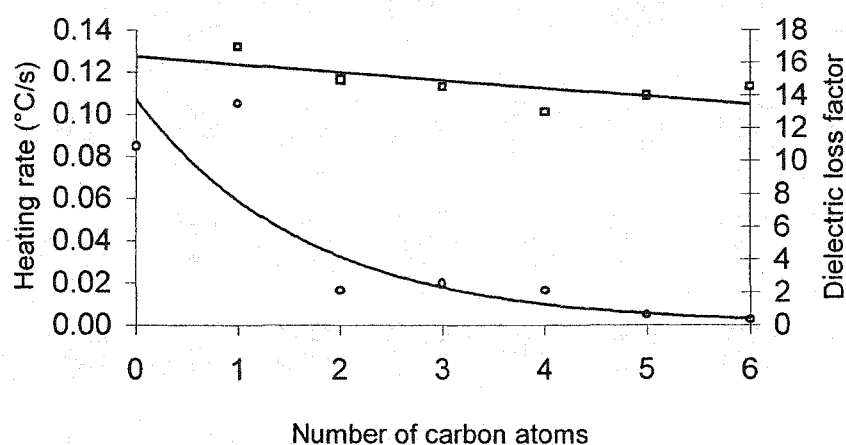


Figure 2.3: (□) Heating rate at a power of 233 W, 2450 MHz and (○) dielectric loss factor at 25 °C of six *n*-alcohols, C_1 to C_6 as a function of the number of carbon atoms in the *n*-alcohol molecules.

2.2 Measurement of Dielectric Properties

There are many technologies to measure the dielectric properties (Klein et al., 1993; Donovan et al., 1993; Dressel et al., 1993; Meda, 1996). Usually, those methods can be classified into two categories: non-resonant methods and resonant methods. The former mainly consists of reflection methods and transmission/reflection methods,

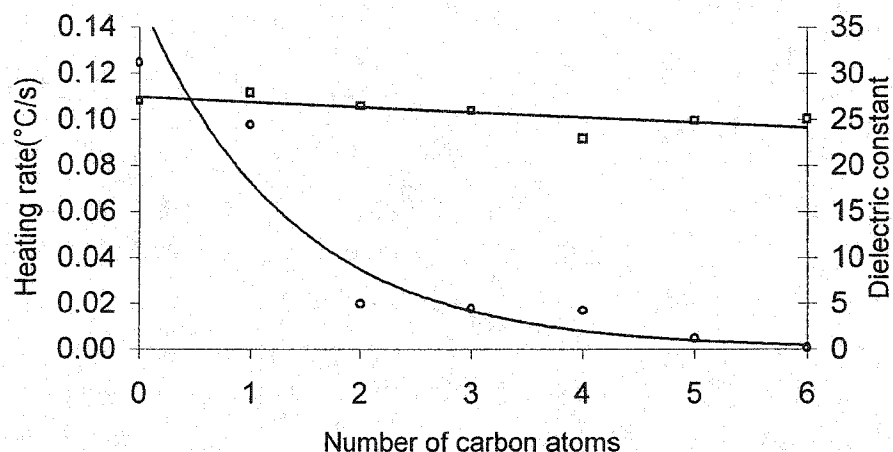


Figure 2.4: (□) Heating rate and (○) dielectric constant at 25 °C of six *n*-alcohols, C₁ to C₆ as a function of the number of carbon atoms in the molecule.

requiring the strict sample preparation during the measurement. The latter mainly includes resonator and resonant perturbation methods, having relatively higher accuracy than non-resonant ones (Chen et al., 1999). The cavity perturbation technique is one of the most widely used due to its simplicity of the measurement set-up, high sensitivity, automated experiment facility, direct evaluation and higher accuracy. It does not require complicated calibration and tuning since a network analyzer can accomplish those analyses. This technique was proposed by Montgomery (1947) and further developed by several researchers in both experimental and theoretical aspects (Waldron, 1960; Champlin and Krongard, 1961; Subramanian and Sobhanadri, 1994). It can be used to measure the dielectric properties of both liquids and solids.

2.2.1 Theory about resonant perturbation

The principle of this technique is based on the changes in the response to resonant cavity under electromagnetic radiation. When a foreign body is introduced into a resonant cavity, the frequency of the resonant (f) and the quality factor (Q) of the cavity change slightly. The change of complex angular frequency ω of a resonant cavity due to the insertion of a sample can be expressed as follows (Waldron, 1969):

$$\frac{\omega_s - \omega_o}{\omega_s} = \frac{\iiint_{V_c} [(\mu_s - \mu_o) H_o \bullet H_s - (\epsilon_s - \epsilon_o) E_o \bullet E_s] dV}{\iiint_{V_c} (\epsilon_o E_o \bullet E_s - \mu_o H_o \bullet H_s) dV} \quad (2.4)$$

Where, subscripts o and s refer to before and after the introduction of the sample, respectively.

ω = complex resonant angular frequency.

ϵ = complex permittivity.

μ = complex magnetic permeability.

H = microwave magnetic field.

E = microwave electric field.

V_c = region enclosed by the cavity.

This equation comes from the assumption that the cavity wall is perfectly conducting and the perturbation is small.

2.2.2 Parameters of cavity perturbation technique

The quality factor Q of the cavity is defined as:

$$Q \equiv \frac{f_o}{\Gamma} = \frac{\omega_o \langle W \rangle}{L} \quad (2.5)$$

Where, $f_o = \omega_o/2\pi$ is the centre frequency and Γ is the bandwidth or full frequency width at half-maximum. f_o and Γ are the two characteristics of the resonant cavity; $\langle W \rangle$ is the time-averaged energy stored in the cavity and L is the energy loss per cycle.

The Q of the cavity is determined by the energy loss per cycle. Three main energy losses are contributed to the Q factor: Ohmic losses in the cavity walls, irradiative losses in the couple device, and losses within the sample placed in the cavity.

For a given measurement frequency, the minimum cavity dimensions are roughly given by $\frac{1}{2}$ the wavelength in each physical dimension (Donoven et al., 1993).

2.2.3 Functions of cavity perturbation technique

Resonant cavities have been widely used successfully to measure the dielectric properties of the materials by measuring the shift in the resonant frequency and the change in the Q factor of the cavity due to the insertion of the sample at the maximum electric field position. This technique can be shown in the Figure 2.5 (Kraszewski and Nelson, 1994). The right peak was produced without the insertion of the sample in the cavity. The left peak was contributed to the sample insertion. The dielectric properties (dielectric constant and loss factor) are given by:

$$\epsilon' = 1 + \frac{(f_o - f_s)V_o}{2kf_oV_s} \quad (2.6)$$

$$\epsilon'' = \frac{V_o}{4k^2V_s} \times \left(\frac{1}{Q_s} - \frac{1}{Q_o} \right) \quad (2.7)$$

Where, subscripts o and s refer to the empty cavity and the cavity loaded with an object at the centre of the cavity, V= volume, f = resonant frequency, Q=Q factor, k= factor dependent upon object shape, orientation and permittivity (Kraszewski and Nelson, 1993).

2.2.4 Some considerations to be taken during the measurement

During the measurement, the most important considerations pertaining to this technique which must be taken in order to get accurate data include (Donoven et al., 1993):

i): The size of the sample ($\lambda > 2a$).

Where, λ is the wavelength of the electromagnetic radiation and $2a$ is the largest sample dimension; the foreign body must be small compared to the spatial variation of the field and its disturbing influence must not be strong enough to force a jump from the unperturbed cavity mode.

ii): $V_s/V_o \ll 1$, Where V_s and V_o are the sample and cavity volumes, respectively.

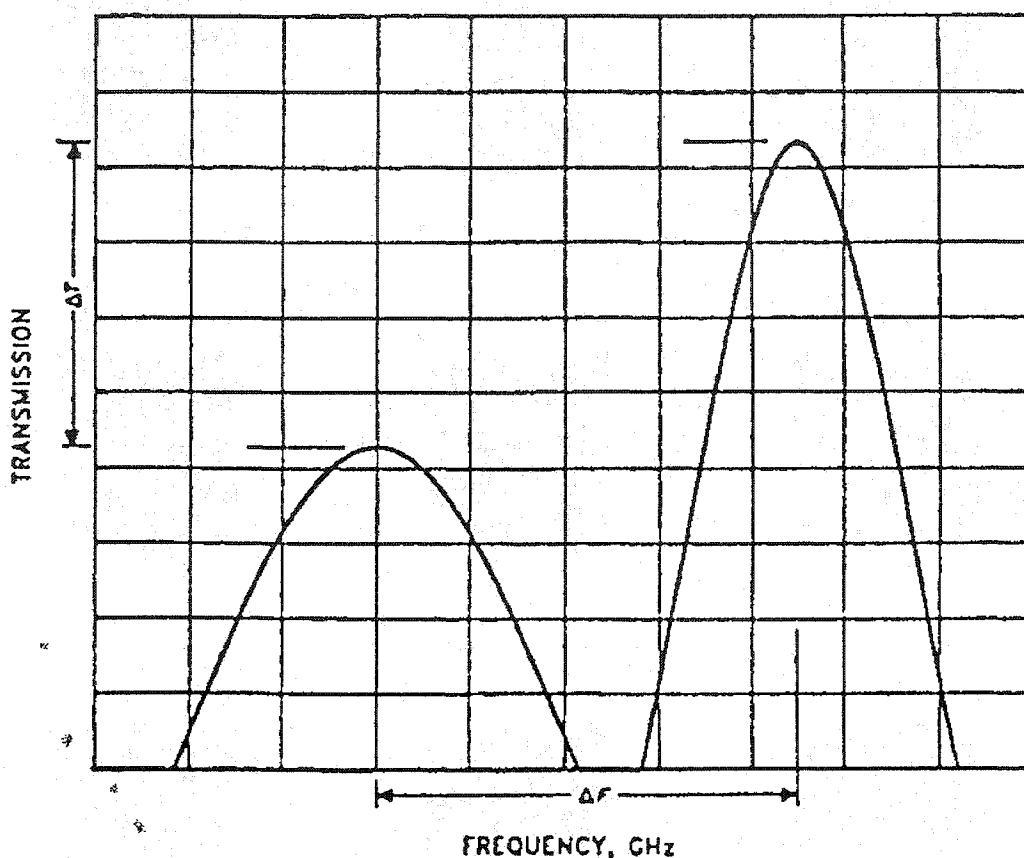


Figure 2.5: Resonant curves for empty cavity (right) and cavity loaded with material (left).

iii): The other factors such as location of the object inside the cavity, mode of operation of the cavity and temperature are also important.

iv): The frequency and the quality factor resolution have to be considered.

2.3 Dielectric Properties of Chemicals and Chemical Reactions

Microwave dielectric heating has attracted interest in the chemical industry due to its ability to provide selective heating, rapidity and to allow local superheating of materials. To apply microwave technology to the chemical reactions, the knowledge of

dielectric properties of chemicals at chosen microwave frequencies is important in fundamental studies of chemical structure, dynamics. It is also important in design, implementation, and control of microwave heating systems for the practical applications of microwave-enhanced chemistry (Kuester, 1994; Mehdizadeh, 1994). The dielectric properties are crucial in microwave heating and in assessing their economic and environmental implications. The dielectric constant and loss factor are necessary to predict various essential microwave-processing parameters such as penetration depth, microwave heating rate and temperature profile within irradiated chemical reactors. Although the database of dielectric properties initiated by von Hippel (1954) and extended by others contains dielectric properties information about materials and foodstuffs, the data for commonly used chemicals for the chemical reactions performed under microwave irradiation are not readily available. In fact, few of data provided were measured at microwave frequencies of 2450 and 915 MHz and at varying temperatures. Most studies focused on the static permittivity (dielectric constant) (ϵ_s) or the limiting high frequency permittivity (ϵ_∞). Data about the static permittivity for the most of the chemicals can be obtained from some handbooks such as Handbook of Chemistry and Physics. When a material absorbs microwaves at 2450 or 915 MHz, the temperature rise profile for the material is dependent on both the dielectric constant and loss factor at these frequencies. The dielectric property investigation focused at 2450 MHz began only after the advent of the microwave assisted chemical reactions (Ayappa et al., 1992). The dielectric properties of acetone/hexane at 2450 MHz were investigated by Punt (1997) using cavity perturbation technique. Lou et al. (1997) also investigated the dielectric properties of various organic solvents and binary solvent mixtures at 21.4 °C over the frequency range of 200 MHz-13.5 GHz using an open-ended coaxial probe. Data about dielectric properties at some specific microwave frequencies for some chemicals are presented in the recent review by Gabriel et al. (1998). In this review, the authors provided the data about some alcohols, nitriles, esters, ketones and chlorhydrocarbons at 2450 MHz.

2.4 Application of Dielectric Properties

Dielectric properties are intrinsic characteristics of the materials explaining the behaviour and degree of the wave-material interaction when exposed to microwave field. They are very important in microwave heating, microwave sensing, process design and application. For example, there are many researchers who have used dielectric properties to measure moisture content of agri-food (Kraszewski et al., 1989; Kraszewski and Nelson 1993, 1994; Meda et al., 1998; Okamura and Zhang, 2000). Nelson et al. (1995) proposed relationships between dielectric properties and maturity of some fruits. Buchner and Barthel (1995) studied the kinetic process in the liquid phase by making use of the dielectric properties of the materials. Rudakov (1997, 1998) used dielectric properties of the solvents to optimize the mobile phase in the high-performance liquid chromatography. In addition, at a fundamental level, the dielectric behaviour of the material can provide the information about molecular interactions and mechanism of molecular processes (Firman, et al., 1991; Lunkenheimer and Loidl, 1996; Suzuki, et al., 1996, 1997; Matsuoka, et al., 1997; Shinyashiki, et al., 1998).

2.5 Mathematical Models for Dielectric Properties

In order to better understand and describe the dielectric properties of the materials, various mathematic models have been proposed. It is possible to use specific models to predict or compute dielectric properties of specific materials according to their compositions.

a) Debye models for polar liquids:

$$\epsilon'_w = \frac{(\epsilon_s - \epsilon_o)}{1 + (\lambda_s / \lambda)^2} + \epsilon_o \quad (2.8)$$

$$\epsilon_w'' = \frac{(\epsilon_s' - \epsilon_o)(\lambda_s / \lambda)}{1 + (\lambda_s / \lambda)^2} \quad (2.9)$$

Where, ϵ_w' and ϵ_w'' are the dielectric constant and loss factor of pure water; ϵ_s and ϵ_o are the static and optical dielectric constant; λ_s and λ are the critical wavelength and wavelength of measurement.

These models were first proposed by Debye following Maxwell equations. It can be used to predict dielectric properties of oil-water and alcohol-water based on pure component properties (Mudgett et al., 1974a).

b) Hasted-Debye models (Hasted et al., 1948):

$$\epsilon_s' = \epsilon_w' - 2\delta C \quad (2.10)$$

$$\epsilon_s'' = \epsilon_w'' + \Lambda C / (1000\omega\epsilon_v) \quad (2.11)$$

Where ϵ_s' and ϵ_s'' are the dielectric constant and loss factor of an aqueous ionic solution; ϵ_w' and ϵ_w'' are the dielectric constant and loss factor of pure water; δ is the average hydration number; Λ is the equivalent conductivity of the solution; ω is the angular frequency and ϵ_v is the dielectric constant of vacuum, C is the dissolved salts concentration.

These models were proposed by Hasted et al. in 1948. The modified Debye model can be used to solve the effects of salt dissociation on water behaviour. Mugett et al. (1974b) used this model to successfully predict dielectric properties of non-fat milk.

c) LLL mixture model: (Looyenga, 1965)

$$\epsilon^{1/3} = v_1 \epsilon_1^{1/3} + v_2 \epsilon_2^{1/3} \quad (2.12)$$

Where, ϵ is permittivity of the mixture; ϵ_1 and ϵ_2 are permittivity components 1 and 2; v_1 and v_2 are the volume fractions of components 1 and 2.

This model has been reliable to estimate permittivities of the mixture (Nelson and You, 1990).

d) Universal model for the mixture of liquids (Thakur et al., 1999)

$$e^{\alpha \varepsilon_m} = v_1 e^{\alpha \varepsilon_1} + v_2 e^{\alpha \varepsilon_2} \quad (2.13)$$

Where, ε_m is permittivity of the mixture; ε_1 and ε_2 are permittivity components 1 and 2; v_1 and v_2 are the volume fractions of components 1 and 2; α is a constant indicating the measure of the interaction among individual phases in the mixture and is unique for a given system.

The model stands on the assumption that non-interactive and distributive in material of dielectrics is a continuous function of permittivity of the material and its derivatives exist in a given interval. Using this model can derive the mixture model proposed by Tinga et al. (1973), and Kraszewski et al. (1976).

2.6 Microwave-assisted Organic Chemical Reactions

Since the advent of the first papers about using microwave energy in the organic synthesis by Giguere et al. (1986) and Gedye et al. (1986), numerous papers and reviews have been published describing the application of microwave dielectric heating in chemistry (<http://www-ang.kfunigraz.ac.at/~kappeco/microlibrary.htm> and the references cited in). Using microwave in the chemical reactions has the following advantages compared to the conventional heating:

- i) Higher heating rates and different temperature profiles (temperature distribution) due to its volumetric heating.
- ii) Selectively heating due to the dielectric properties of the materials.

In the beginning, most of the microwave-assisted chemical reactions were performed with an organic solvent in sealed vessels using domestic microwave ovens; however, the present trend is to carry out reactions without any solvents. It is possible to use dielectric heating method without solvents to obtain chemicals at higher yields in short reaction time, thus leading to minimum waste. It is normal for us to notice several papers about microwave-assisted organic synthesis appearing in the recognized journals

each week. The variety of work, which has been carried out in microwave field, includes analysis, organic synthesis, extraction and digestion, ceramic processing, and pyrolysis (<http://www.ed.ac.uk/~ah05/microwave.html> and references cited in). Especially, interest in microwave application in chemistry, drug discovery from academic, governmental, company, and industrial laboratories has increased in recent years. Esterification (Majetich and Hicks, 1995) and Maillard reactions (Yaylayan, 1996) are typical reactions, which can also be carried out under microwave irradiation.

2.6.1 Microwave-assisted esterification

2.6.1.1 The present status of microwave-assisted esterification

Esters have been served in a variety of industrial applications (Tedder et al., 1975). For instance, *p*-hydroxybenzoic acid esters have been widely used as antimicrobial agents in cosmetics due to their broad antimicrobial spectrum, relative low toxicity, good stability and no volatility (Cantwell, 1976). The suitable catalyst is essential for esterification whether it is performed through conventional heating or microwave heating. Under microwave irradiation, the catalysts for the esterification include sulfuric acid, PTSA (toluenesulfonic acid), inorganic acid such as phospho-tungstic acid and inorganic salt such as FeCl_3 and phase transfer catalyst hexadecyltrimethylammonium bromide (HDTMAB). Esterifications can be performed in dry media (without solvent) or liquid media (with solvent or one excess reactant (liquid)) under microwave irradiation. Under dry media, it can take advantage of rate enhancements because of thermal effects resulting from microwave dielectric heating, and displacements of equilibriums by removal of volatile polar molecules such as water and small alcohols. These dry media include alumina (Loupy et al., 1993; Su et al., 2000; Zhou, 2001; Gasgnier et al., 2001), polymer-support (Stadler and Kappe, 2001), active carbon-support (Li et al., 2000; Fan et al., 1999, 2000), montmorillonite clay (Esveld et al., 2000). Perez et al. (2001) performed the esterification of fusel oil using a solvent-free microwave method and *p*-TsOH or $\text{H}_3\text{PW}_2\text{O}_{40}$ (HPW) as catalysts. Esterification reactions under microwave irradiation in liquid media were often performed when one of the reactants such as alcohol, was liquid. In fact, the first microwave-assisted esterification reactions were performed in liquid media (Gedye et al., 1986). Majetich and Hicks (1995) have studied the esterification of

the diacid and methanol using concentrated sulfuric acid as a catalyst under microwave irradiation. Chen and co-workers (1990) developed a continuous-flow apparatus that pumped the reagents through reaction coil in commercial microwave oven. Li et al. (1997) also used a continuous flow apparatus to study the esterification of the low carbon carboxylic acid with propan-1-ol. Liu et al. (1992) presented that the esterification of the $\text{Me}(\text{CH}_2)_n\text{CO}_2\text{H}$ ($n = 2, 3, 5$) with butanol using Lewis acid $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ as an acid-catalyst to get esters $\text{Me}(\text{CH}_2)_n\text{CO}_2\text{Bu}$. Four salicylate esters were synthesized under microwave power 560W at normal pressures in 22 minutes with the yield between 88.7% and 94%. The reaction rate was at least 14 times as fast as with classical conditions (Fan et al., 1998). Zhang et al. (1998) and Chen et al. (1993) reported that p-hydroxybenzoic acid was refluxed with ROH ($\text{R} = \text{Et}, \text{n-Pr}, \text{Bu}$) employing concentrated sulfuric acid as a catalyst under microwave irradiation for 30 minutes to give 87-93.5% corresponding esters. The esterification of benzoic acid with ethanol was studied in a continuous tubular flow reactor heated by microwaves. In this study, the authors employed sulfuric acid and ion exchange resins as the catalyst (Pipus et al., 1998, 1999). The butyl gallate was synthesized to produce 87% yield by esterification of the gallic acid and butanol with p-methylbenzenesulfonic acid as the catalyst under microwave irradiation (Yuan et al., 1998). Normal-butyl acrylate was prepared through esterification of the acrylic acid and butanol under microwave irradiation with solid super acid $\text{TiO}_2/\text{SO}_4^{2-}$ as a catalyst. The 86.8% yield was obtained in 120s under microwave irradiation (Chen and Peng, 1999).

2.6.1.2 Factors affecting esterification and superheating

There are many factors which have influence on a specific chemical reaction performed at normal pressure. Generally, they involve reactivity of each reactant, the concentration of each reactant, the reaction temperature, and the reaction time. For reactions under microwave irradiation, additional factors include irradiation power and dielectric properties of each compound. Gedye et al., (1986) found that there was an inverse relationship between rate enhancement and the boiling point of the solvent when using microwave irradiation to synthesize methyl, propyl, and butyl benzoic acid esters. The differences between the same acids with different alcohols are shown in Table 2.3.

Table 2.3: Microwave-enhanced esterification reactions in sealed tube (Gedye et al., 1986).

Compound synthesized	Procedure followed	Reaction time	Recovery*	
			Product	Reagent
Esterification of benzoic acid with methanol				
C ₆ H ₅ COOCH ₃	Classical	8 hrs	74%	19%
C ₆ H ₅ COOCH ₃	Microwave	5 min.	76%	11%
Esterification of benzoic acid with propanol				
C ₆ H ₅ COOC ₃ H ₇	Classical	7.5 hrs	89%	7%
C ₆ H ₅ COOC ₃ H ₇	Microwave	18 min.	86%	11%
Esterification of benzoic acid with n-butanol				
C ₆ H ₅ COOC ₄ H ₉	Classical	1 hrs	82%	12%
C ₆ H ₅ COOC ₄ H ₉	Microwave	7.5 min.	79%	17%

*: recovery values are based on isolated yields and represent the average of at least two experiments

As we know, lower carbon alcohols having higher dielectric properties but with relatively lower molecular weight will tend to display a capacity for superheating under microwave irradiation (Table 2.4). Superheating under microwave irradiation has been investigated by a number of authors (Bond et al., 1991; Saillard et al., 1995), and a model was proposed for the behavior based on the mechanism of nucleate bubble formation, which expressed the kinetic aspects of boiling (Baghurst and Mingos, 1992). Since microwave heating plays an important role in physic-chemical properties of the chemicals, they have to be considered in the study.

Saillard et al. (1995) have investigated superheating of ethyl and methyl alcohols under microwaves in a monomode cavity. They found that under microwave heating after a rapid increase of the temperature, a plateau region of constant temperature was observed

as the liquid began to reflux, while under conventional heating no superheating occurred (Figure 2.6).

Table 2.4: Superheating of solvents measured by a variety of methods (temperatures are in °C).

Solvent	Boilin g point	Dielectric constant ^a	Xylene thermometer ^b	Fluoro-optic thermometer ^b	Fiber optic probe ^c	Thermal Imaging ^b
Water	100	78.3	104(+4)	104(+4)		105(+5)
Methanol	65	32.7	78(+13)	84(+19)	71(+6)	84(+19)
Ethanol	79	24.7	90(+11)	103(+24)	91(+12)	
2-Propanol	82		87(+5)	100(+18)		108(+26)

^a (Kingston and Stephen, 1997); ^b (Whittaker and Mingos, 1994); ^c (Saillard et al., 1995).

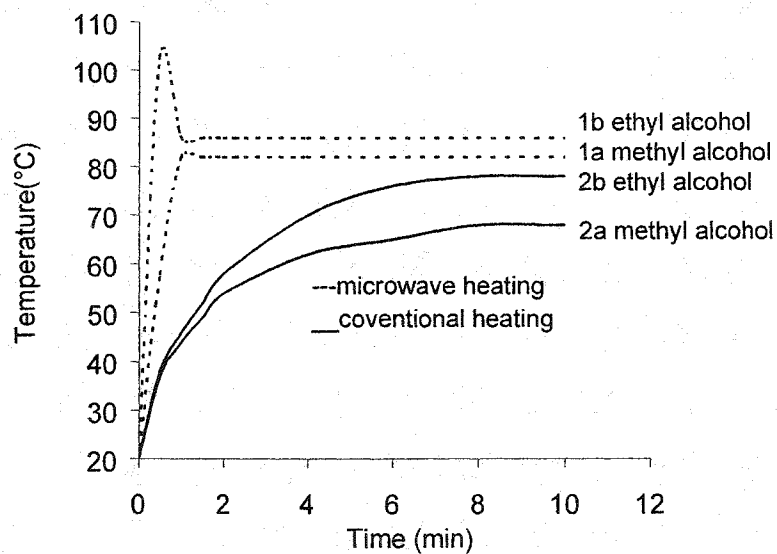


Figure 2.6: Temperature profiles

2.6.1.3 Reason for microwave-assisted esterification

Superheating is widely believed to be responsible for the rate and yield increase, which accompany many liquid phase reactions. Reports by a number of researchers have suggested other peculiarities when microwaves are responsible for enhanced reactions and esterification compared to without microwave enhancement.

For the microwave-enhanced esterification, an explanation for rate enhancement is that the irradiation leads to a fast increase in reaction temperature rather than to a specific non-thermal microwave effect (Stadler and Kappe, 2001). Among the results about microwave-enhanced esterification, Pollington et al. (1991) found that in carefully controlled systems, the rates of esterification of 1-propanol with ethanoic acid are almost similar in both with and without microwave irradiation (Figure 2.7). In the following year, Raner and Strauss (1992) reported rates of esterification of 2,4,6 -trimethylbenzoic acid with 2-propanol to be similar both under microwave reactor and in the oil bath

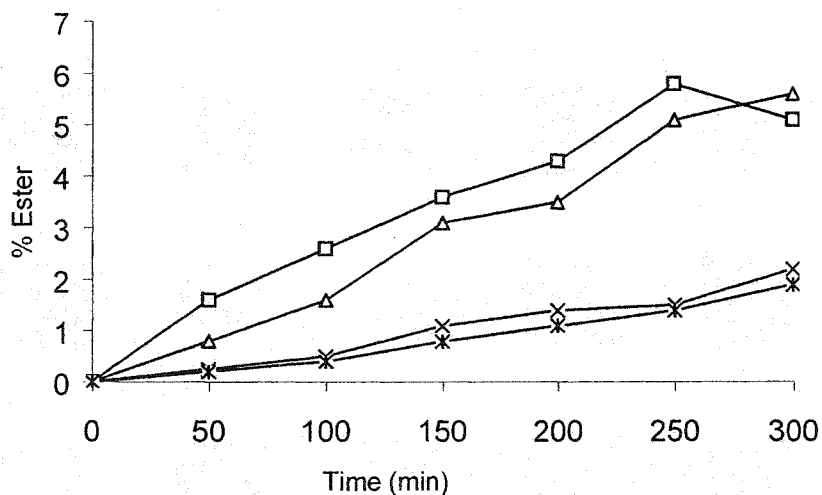


Figure 2.7: Concentration of ester as a function of time during heating under reflux at atmospheric pressure: (□): H₂SO₄ catalyst conventional heating; (Δ): H₂SO₄ catalyst microwave heating; (×): silica catalyst conventional heating; (*): silica catalyst microwave heating.

experiments. The final yield of ester depends only on the nature of the temperature profile and not on the mode of heating. Li et al. (1996,1997) have investigated esterification reactions of ethylcellosolve and acetic acid with concentrated sulfuric acid as a catalyst. They found that the rate of esterification had been accelerated by microwave irradiation due to the fact that the rate of increase in temperature under microwave irradiation is faster than that with conventional heating methods. But if the rate of microwave heating is very close to that with conventional heating methods, no microwave rate enhancement was observed. If the temperature of reflux reaction and the rate of reflux under microwave irradiation are of the same value as the conventional heating methods, then there will be no microwave rate enhancement. They also investigated the effects of dielectric constant of reactants on the rate of esterification reactions by microwave irradiation in a continuous flow procedure. They found dielectric constant of the reactants to be one of the substantial factors to have an influence on the reaction rate (Figure 2.8). By adding a small amount of extra special substance with larger dielectric constant into the reaction system of lower dielectric constant, the reaction rate increased (Figure 2.9). Within experimental error, identical yields were also observed for the microwave heating and conventionally heated reactions when the reactions were heated to approaching boiling point.

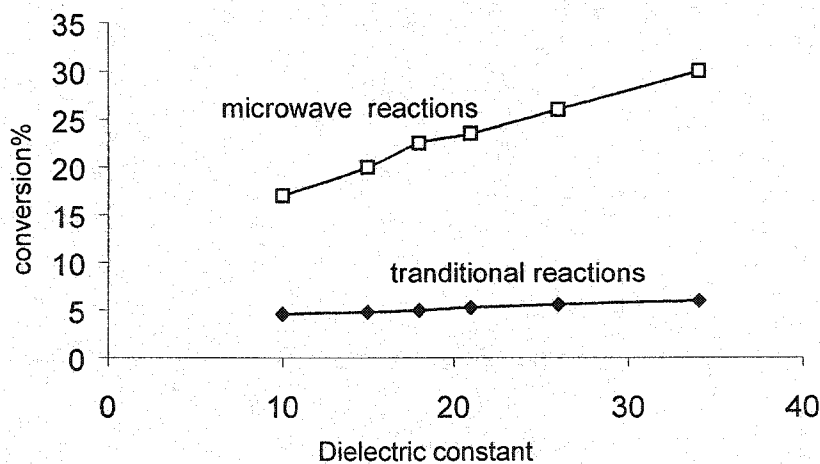


Figure 2.8: The comparison of conversion vs dielectric constant of different alcohols under microwave heating and traditional heating.

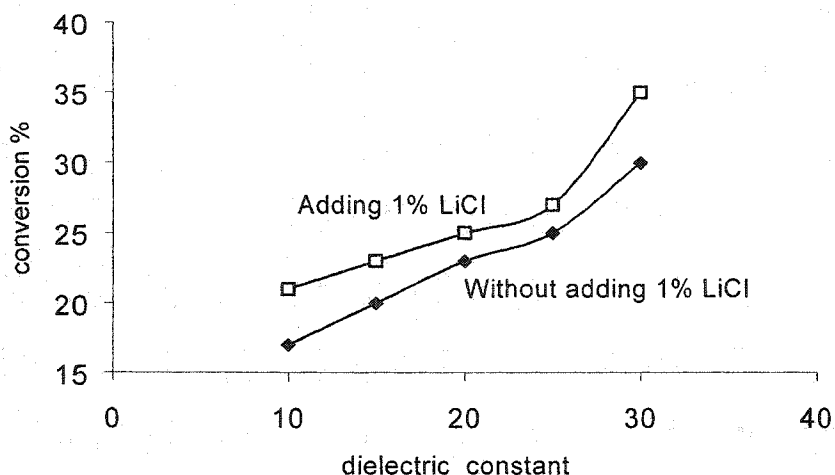


Figure 2.9: The comparison of conversion vs dielectric constant of different alcohols with or without adding LiCl under microwave heating.

2.6.2 Microwave-enhanced Maillard reaction

Maillard reaction, which was named after its inventor, Lois-Camille Maillard, is one of the major reactions linked to the formation of food flavors and colors during thermal processing. Because of its importance in the determination of color and flavor properties of foods, it plays a crucial role in food chemistry and food processing. (Feather, 1989; Ames, 1990; Bailey et al., 1995; Ho, 1996; Ikan, 1996; Yaylayan, 1996). Although microwave ovens became popular in the 1970's, the market for microwave-processed food became attractive only in the 1980's (Decareau, 1992). It was forecast that in the 1990's the percentage of U. S. households owning at least one microwave oven to exceed 80% (Shaath and Azzo, 1989) due to the fact that it is easy, fast and convenient to cook compared to the conventional cooking methods. However, microwave-cooked foods often lead to a lack of browning and desirable flavors. This disadvantage has prompted researchers to do some investigations about microwave-enhanced Maillard reaction in the food process. A recent review about Maillard reaction under microwave irradiation has been given by Yaylayan (1996).

The Maillard reaction is a cascade of complex reactions involving the interaction initiated between the terminal α and ϵ -amino group of lysine residue in peptides or protein and the carbonyl moiety of reducing sugars. It was divided into three stages: early,

advanced and final reaction, which can be characterized by absorption spectra and molecular weights (Wijewickreme et al., 1997). The first step in the Maillard reaction is the formation of a Schiff's base (aldimine) between the carbonyl group of a reducing sugar and the free amino group of an amino acid, peptide or protein. The second step is rearrangement of the Schiff's base to Amadori compounds, which are very reactive intermediates. The third step is the further reaction of Amadori compounds by several pathways such as enolization, dehydration, aldol condensations and Strecker degradation to form a bulk of compounds leading to many significant flavors.

Barbiroli et al. (1978) found that the amount of the aminodeoxyketose formed in microwave oven baking was larger than that in the traditional and IR oven. However, the subject about microwave enhanced Maillard reaction was really encouraged by the fact that a wide range of reactions can be completed under microwave irradiation in a much shorter period of time compared to the conventional heating modes (Gedye et al., 1986; Giguere et al., 1986).

Parameters affecting microwave-enhanced Maillard reaction

Maillard reaction under microwave irradiation is strongly affected by the reaction conditions. The most important factors are the concentration and nature of the primary reactants; temperature of heating, irradiation power supplied, moisture content, pH (acidity or basicity), pressure, irradiation time, water activity, metal ions, and media (solvent).

The effects of pH on the production of heterocyclic flavor compounds in the D-glucose/L-cysteine model system under microwave irradiation have been investigated by Yeo and Shibamoto (1991a). They found that the total volatiles generated from this model system increased with the pH values. It is the first time to detect a nutty, meaty, and roasted aroma, 2-methylthiazolidine in a sugar/ amino acid model system. They suggested pH value to be responsible for this result, because the production of volatile in the Maillard system under microwave irradiation was base-catalyzed reactions. Zamora and Hidalgo (1992, 1995) investigated the influence of pH on the color, fluorescence, product of a lysine/(E)-4,5-epoxy-(E)-2-heptenal model system under microwave irradiation. They found that both color and fluorescence depended on the pH. The production of 1-

alkylpyrroles was mainly controlled by the pH. However, they did not mention that the dielectric properties of the reactants were dependent on the pH.

Zamora and Hidalgo (1992) have studied the influence of different mole value of sodium chloride on a lysine/(E)-4,5-epoxy- (E)-2-heptenal model system using microwave energy. Yeo and Shibamoto (1991b) have also studied the influence of the electrolytes on the D-glucose/L-cysteine system. An enhancement in flavor production was observed due to the use of the electrolytes in the microwave-irradiation model system, but different electrolytes have different results. Sodium chloride promoted the amount of volatiles by 200% compared to the use of ferrous chloride. A suggestion that the dielectric properties of the electrolyte solutions may result in an overall increase in the generation of volatiles under microwave irradiation was proposed, but they presented no details about the dielectric properties of the mixture of the reactants and salt.

The effects of moisture content on the production of heterocyclic flavor compounds in the D-glucose/L-cysteine model system under microwave irradiation have been investigated by Yeo and Shibamoto (1991c). They found that the total volatile generated from this model system increased with moisture content to a maximum at 11% moisture, while above 11% moisture, the total volatiles decreased with moisture content. Maillard reaction of different amino acids with glucose in different media such as propylene glycol or glycerol has been investigated by Yu et al. (1998) and the changes in the color, appearance, and aroma from the reaction were compared as well.

Keyhani (1997) have investigated the influence of concentration of the reactants on the Aldose/Glycine, D-glucose/L-alanine Maillard reaction model systems under microwave irradiation. In the D-glucose/ glycine model system, a new compound was produced when the ratio of glucose/lysine was 1/3. Zamora and Hidalgo (1992, 1995) investigated the effect of epoxyheptenal/lysine ratio on color, fluorescence and the products of the Maillard reaction model system lysine/(E)-4, 5-epoxy-(E)-2-heptenal. The influence of irradiation time on the product was discussed as well, but the influence of concentration of the reactants on the dielectric properties of the reaction was not mentioned.

CONNECTING TEXT

A comprehensive review of literature demonstrated a need for knowledge of dielectric properties of material, especially for the chemicals, which plays a crucial role in the microwave-assisted chemistry. The present study seeks to establish the relationship between dielectric properties of the chemicals with their concentration, temperature and to find the application of dielectric properties in the chemical reaction.

In Chapter III, the dielectric properties of the alcohols at microwave frequencies of 2450 and 915 MHz are investigated. The effect of temperature on the dielectric properties is discussed. The relationship between dielectric properties and the temperature, half-penetration depth is demonstrated as well.

The material presented in this chapter has already appeared in a peer reviewed journal (see details of publication below):

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2001. Dielectric properties of alcohols (C₁-C₅) at 2450 and 915 MHz. *Journal of molecular liquids*. 94 (1): 51-60.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

III. DIELECTRIC PROPERTIES OF ALCOHOLS (C₁-C₅) AT 2450 AND 915 MHz

3.1 Abstract

The dielectric properties of alcohols (C₁-C₅) at 2450 and 915 MHz were measured at different temperatures using a cavity perturbation technique. Dielectric properties were shown to be dependent on temperature, frequency and alcohol type. The dielectric constants increased with temperature at both frequencies; however, there were significant differences in dielectric loss factor. Linear and quadratic equations were developed for each type of alcohol to relate changes in dielectric constant, dielectric loss factor or half-power penetration depth with temperature. These relationships are useful in estimating the volumetric heating of alcohols by microwave energy at 2450 or 915 MHz, analyzing the differentially thermal transition in materials, selecting solvents and shedding some light on microwave-assisted chemical reactions.

3.2 Introduction

An understanding of the frequency or temperature-dependent dielectric properties of alcohols is important both in fundamental studies of alcohol structure and dynamics and in practical applications of microwave-enhanced chemistry. The dielectric properties are crucial in microwave processing applications and in assessing their economic and environmental implications. Important dielectric properties, the relative dielectric constant and dielectric loss factor, are necessary to predict various essential microwave-processing parameters such as half-power penetration depth and microwave heating rate (Copson, 1975; Mudgett, 1986; Decareau, 1992). In microwave-assisted chemical reactions in the presence of alcohols, the availability of quantitative data on dielectric properties of alcohols, or methods for their prediction, are essential for the design, implementation, and development of microwave-heated processing. One area of current interest is the heating of chemicals by microwave energy, which appears to be promising and shows some advantages over conventional heating methods such as oil bath, electric

oven, and heating mantle. The advantages include faster heating rate, reduction of reaction time, possibility for remote operation, and the ability to changes in temperature profiles, chemical reactivity, product selectivity and quality (Mingos and Baghurst, 1991; Morcuende et al., 1996; Avalos et al., 1999; Cleophax et al., 2000). Since most applications in microwave-assisted chemical reactions involve microwave frequencies of 2450 and 915 MHz, it is necessary to investigate the dielectric properties of the chemical compounds at both frequencies.

Many investigations on the dielectric properties of alcohols exist, but none of them have focused on both 2450 and 915 MHz frequencies and different temperatures. Some studies have focused on the static permittivity (dielectric constant) (ϵ_0) or the limiting high frequency permittivity (ϵ_∞) (Danhauser and Cole, 1955; Chahine and Bose, 1976; Nyshadham et al., 1992; Lee, 1998). However, these dielectric properties do not allow the selection of solvents or the study of the underlying mechanisms of microwave-assisted chemistry. The misconception that solvents possessing higher dielectric constants heat rapidly while those with lower dielectric constants heat slowly under microwave irradiation has misled many people in their selection of heating media for chemical reaction or extraction in a microwave field. When a material absorbs microwaves at 2450 or 915 MHz, the temperature rise profile for the material is dependent on both dielectric constant and dielectric loss factor at these frequencies. However, it is not mainly dependent on those dielectric constants mentioned in the literature, which are static permittivities (Garg and Smyth, 1965; Bottreau et al., 1977; Jordan et al., 1978; Douglas and Marcel, 1987; Schweitzer and Morris, 2000). As different alcohols differentially affect the heating characteristics of material during microwave heating, the selection of an alcohol is the most influential factor on the heating rate of microwave-assisted chemical reactions. Unfortunately, data regarding both dielectric constant and dielectric loss factor at 2450 and 915 MHz at elevated temperatures are rare or non-existent. The dielectric behavior of a series of low molecular weight alcohols when exposed to microwaves at different temperatures will not only be useful for microwave-assisted synthesis, but also can help in our understanding of the mechanisms of microwave-enhanced chemical reactions and associated differential temperature distributions. This will shed some light on the reasons for the enhanced-chemical reaction under microwave irradiation.

This study is sought to compare the dielectric properties of alcohols at 2450 and 915 MHz using a cavity perturbation technique. In order to predict thermal effects of the microwave heat processing, equations that correlate the effects of variations in temperature on the dielectric constant and loss factor were determined in this study. The half-power penetration depth is also discussed due to its importance in microwave heating rate. The models for dielectric properties and half-power penetration depth were obtained using the experimental data generated here.

3.3 Materials & Methods

3.3.1 Materials

All alcohols were obtained commercially, were of analytical grade reagent (AR) and were used without further treatment. The alcohols include methanol, 1-propanol, 1-butanol, 1-amyl-ol. Ethanol refers to the mixture of 90% ethanol and 10% methanol.

3.3.2 Dielectric properties measurement

Dielectric properties of alcohols and water were measured by using a cavity perturbation technique at 2450 and 915 MHz. Measurement required a dielectric analyzer (Gautel Inc.), a PC, measurement cavity, and heating/cooling unit (Isotemp 1013S, Fisher Scientific Inc.) (Figure 3.1). Before starting measurements, the calibration was verified by taking measurements on a standard liquid (water) with known dielectric properties. The sample was confined in a 10 μ l sample holder (Borosilicate glass Fisherbrand Micropipets). The heating/cooling unit monitored sample temperature. Dielectric measurements were taken in the temperature range of 25-85°C at 10°C intervals. The following equations were used to calculate ϵ' (dielectric constant) and ϵ'' (dielectric loss factor) using SYNS98 (Meda, 1996):

$$\epsilon' = 1 + 0.539 \left(\frac{V_o}{V_s} \right) (\Delta f) \quad (3.1)$$

$$\epsilon'' = 0.269 \left(\frac{V_o}{V_s} \right) \left(\frac{1}{Q_s} - \frac{1}{Q_o} \right) \quad (3.2)$$

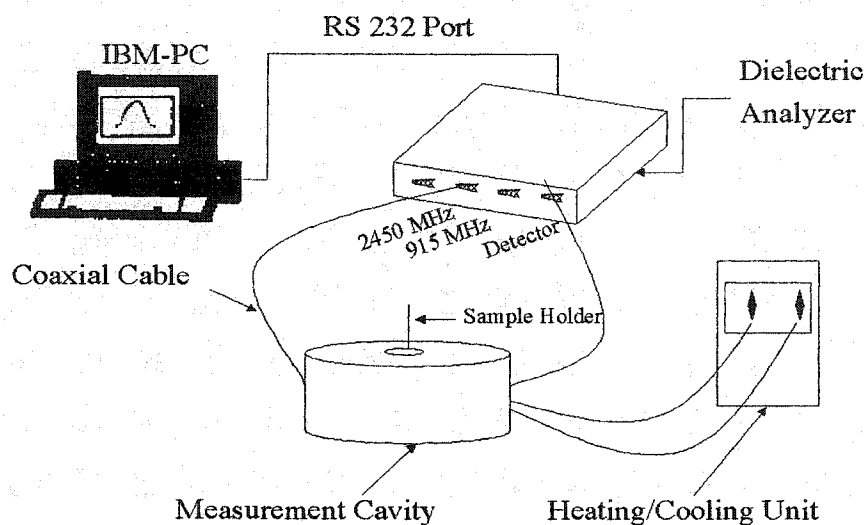


Figure 3.1: Dielectric property measurement set-up.

$$\Delta f = \frac{f_o - f_s}{f_s} \quad (3.3)$$

Where: V_s and V_o are the volumes of the sample and the cavity, respectively; f_o and f_s are the resonant frequencies of the empty and sample loaded cavity, respectively; Q_o and Q_s are the quality factors of the empty and sample loaded cavity, respectively.

Analysis of variance was used to determine significant differences among the alcohols at both frequencies. Three samples were used for each alcohol. Regressions obtained for each alcohol were used to relate dielectric constant, loss factor, and half-power penetration depth to temperature using PROC GLM in SAS (Version 6.12 for Windows 98).

3.4 Results & Discussion

3.4.1 Dielectric constant of alcohols

The dielectric constants of all tested alcohols measured at 2450 and 915 MHz increase with increasing temperature (Figures 3.2 and 3.3). The dielectric constant at 2450 MHz is lower than that at 915 MHz. Methanol has the highest dielectric constant among the alcohols tested within the range of temperatures tested. As the number of carbon atoms in the molecule increases, the dielectric constant decreases. However, very little difference in dielectric constant is found between both 1-butanol and 1-amyl-ol at 2450 MHz (Figure 3.2) and between 1-propanol, 1-butanol, and 1-amyl-ol at 915 MHz (Figure 3.3). This suggests that C₃-C₅ alcohols should be representatives of the behavior

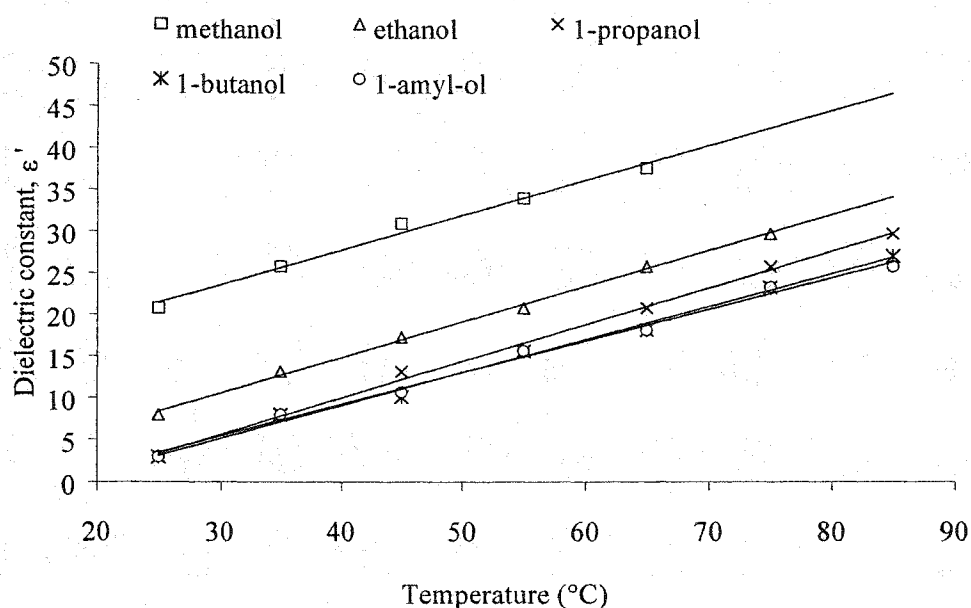


Figure 3.2: Dielectric constant of alcohols vs temperature at 2450 MHz.

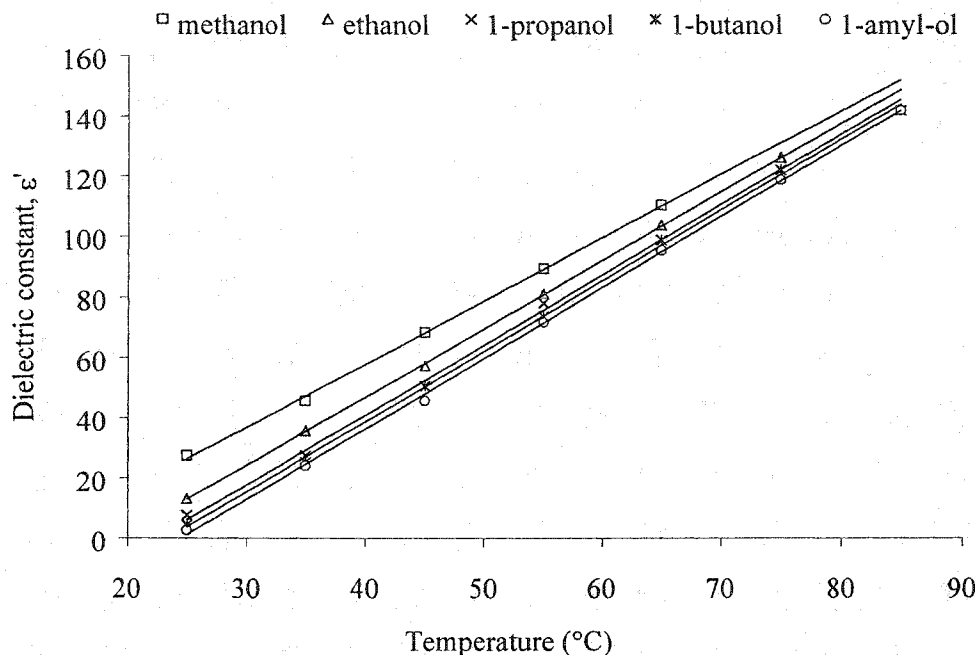


Figure 3.3: Dielectric constant of alcohols vs temperature at 915 MHz.

of the dielectric constant at different temperatures for the other liquid aliphatic alcohols with over 5 carbon atoms. The results for 1-butanol and ethanol at 2450 MHz are in agreement with the results reported by Gabriel et al. (1998). However, in Gabriels' paper, the dielectric constant of methanol decreases with an increase in temperature (30-60°C). The behavior of 1-propanol, 1-amyl-ol at 2450 MHz and of all the alcohols tested at 915 MHz in the temperature range of 25-85°C has not been reported elsewhere. Although the dielectric constants increase with increasing temperature at both frequencies, the rate of increase in the tested temperature range is lower at 2450 MHz than it is at 915 MHz. In our study, both Figures 3.2 and 3.3 show a linear relationship between the dielectric constant and the temperature.

3.4.2 Dielectric loss factor of alcohols

The corresponding temperature dependence for the dielectric loss factor of alcohols at both frequencies is shown in Figures 3.4 and 3.5. The dielectric loss factors for methanol, ethanol at 2450 MHz are higher than those at 915 MHz. At 2450 MHz, methanol has the highest dielectric loss factor among those alcohols tested at all

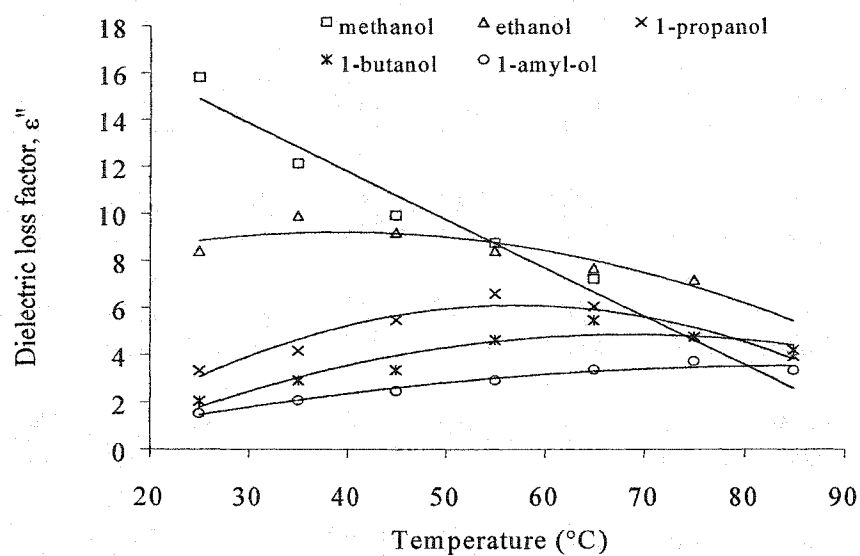


Figure 3.4: Dielectric loss factor of alcohols vs temperature at 2450 MHz.

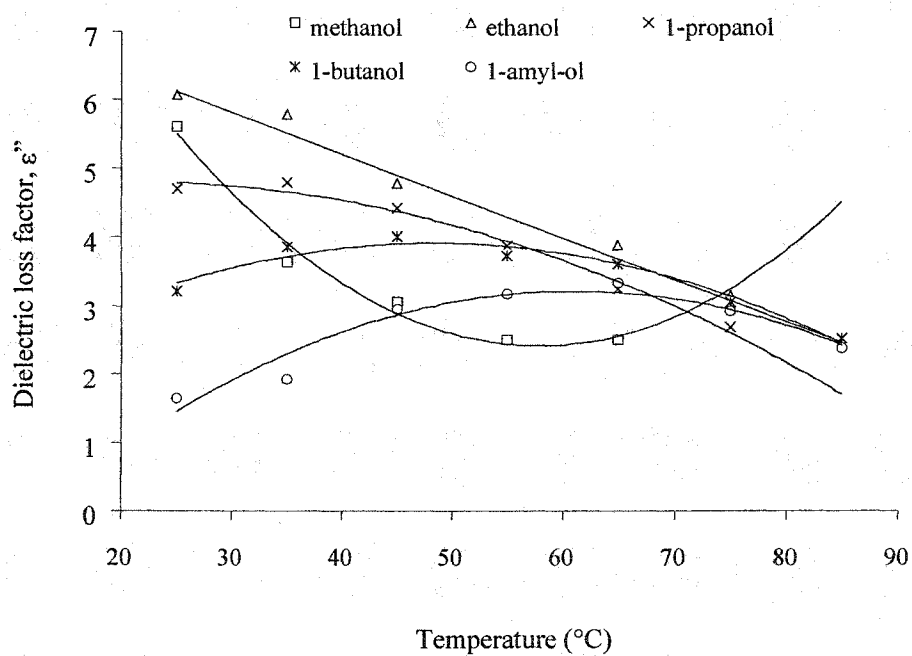


Figure 3.5: Dielectric loss factor of alcohols vs temperature at 915 MHz.

temperatures tested while ethanol has the highest value at 915 MHz. At 2450 MHz, the dielectric loss factor of methanol decreases with an increase in temperature and this observation is in good agreement with other results reported (Gabriel et al., 1998; Palacios et al., 1996). The dielectric loss factor of ethanol first increases with temperature and then decreases, this observation is the same as the result reported by Gabriel et al. (1998), but it is different from the results reported by Palacios et al., (1996). In Palacios' paper, the dielectric loss factor for six chromatographic grade alcohols C₁ to C₆ at 2450 MHz decreases smoothly in the temperature range 14-75°C. In our study, however, the dielectric loss factors of the other alcohols first increase with temperature and then decrease (Figure 3.4 and Figure 3.5). This observation differs with previously reported results (Gabriel et al., 1998; Palacios et al., 1996). The different behavior observed may be a result of the differences in chemical structure at the molecular level among those alcohols or of the experimental protocol. Interestingly, when temperature rises to 65 °C, both 1-propanol and 1-butanol have similar values for the dielectric loss factor at 2450 MHz (Figure 3.4).

3.4.3 Models for predicting dielectric properties

In Figures 3.2-3.5, the points represent the experimental data and the lines are the best-fit curves to the experimental points. Linear and quadratic equations are used to express the temperature dependency of the dielectric constant and dielectric loss factor, respectively.

$$\varepsilon' = a * T + b \quad (3.4)$$

$$\varepsilon'' = c * T^2 + d * T + e \quad (3.5)$$

Where, T indicates the temperature of the alcohol in °C which is below the boiling point of the alcohol and the parameters a, b, c, d, e in equations (3.4) and (3.5) were determined by the least square method and are summarized in Tables 3.1 and 3.2.

The behaviour of dielectric constant with temperature at both frequencies can be predicted using the linear equation model. However, there are some significant differences in the behaviour of dielectric loss factor at both frequencies. At 2450 MHz, only the dielectric loss factor of 1-propanol quadratically varied with temperature. At 915 MHz, the behaviour of dielectric loss factor for all alcohols except ethanol with temperature shows a good quadratic relationship.

Table 3.1: Regression equation constants and coefficients of determination (r^2) of the equations for alcohols and water between 25-85 °C at 2450 MHz.

Alcohol	Dielectric constant		Coeff.	Dielectric loss factor			Coeff.
	aT + b			cT ² + dT + e			
	a	b	r ²	c	d	e	R ²
Methanol	0.417 ^{***}	10.99 ^{***}	0.988	.004 [*]	-.549 ^{***}	26.99 ^{***}	0.993
Ethanol	0.429 ^{***}	-2.37 ^{**}	0.997	-.002 [*]	0.142 [*]	6.43 [*]	0.791
1-propanol	0.441 ^{***}	-7.71 ^{***}	0.993	-.003 ^{***}	.338 ^{***}	-3.56 [*]	0.907
1-butanol	0.395 ^{***}	-6.77 ^{***}	0.993	-.002 [*]	.224 ^{**}	-2.802 [*]	0.893
1-amyl-ol	0.380 ^{***}	-6.03 ^{***}	0.993	-.0006 [*]	.098 ^{**}	-.634 [*]	0.959
Water	0.076 ^{***}	74.36 ^{***}	0.800	0.003 ^{**}	-.458 ^{***}	20.98 ^{***}	0.955

***: significant at 0.0001; **: significant at 0.001; *: significant at 0.01.

Table 3.2: Regression equation constants and coefficients of determination (r^2) of the equations for alcohols and water between 25-85 °C at 915 MHz.

Alcohol	Dielectric constant		Coeff.	Dielectric loss factor			Coeff.
	aT + b			cT ² + dT + e			
	a	b	r ²	c	b	e	R ²
Methanol	2.094 ^{***}	-25.9 ^{***}	0.998	.0028 ^{***}	-.330 ^{***}	11.99 ^{***}	0.943
Ethanol	2.264 ^{***}	-43.6 ^{***}	0.999	.0006 [*]	2.207 ^{***}	-42.40 ^{***}	0.999
1-propanol	2.276 ^{***}	-50.8 ^{***}	0.996	-.001 ^{***}	.015 ^{***}	4.17 ^{***}	0.936
1-butanol	2.333 ^{***}	-54.5 ^{***}	0.999	-.001 ^{***}	.105 ^{***}	1.38 ^{***}	0.769
1-amyl-ol	2.343 ^{***}	-57.4 ^{***}	0.999	-.001 ^{***}	.164 ^{***}	-1.80 ^{***}	0.762
Water	1.992 ^{***}	18.9 ^{***}	0.998	.001 ^{***}	-.157 ^{***}	6.32 ^{***}	0.999

***: significant at 0.0001; **: significant at 0.001; *: significant at 0.01.

3.4.4 Half-power penetration of alcohols and water

The half-power penetration depth is an effective and convenient measure to compare the relative microwave absorbing characteristics of materials and to explain the effects of the dielectric properties and geometry on microwave heating (Decareau, 1992; Schiffman, 1986). The half power penetration depth in centimeters ($d_{p/2}$) is calculated from the measured dielectric properties by the following equation:

$$d_{\frac{P}{2}} = \frac{0.078\lambda_0}{\sqrt{\epsilon'(\sqrt{1 + (\frac{\epsilon''}{\epsilon'})^2} - 1)}} \quad (3.6)$$

Where: λ_0 is the wavelength in free space; ϵ' is the dielectric constant and ϵ'' is the dielectric loss factor.

The half-power penetration depths were calculated for water and five alcohols from the dielectric properties measured at different temperatures and are shown in Figures 3.6 and 3.7. The half-power penetration depth at 2450 MHz is shorter than that at 915 MHz. At both frequencies, ethanol has the shortest half-power penetration depth. The half-power penetration depths for all alcohols are shorter than that of water. This suggests that the microwave-heating rate of ethanol, methanol, 1-propanol, 1-butanol, 1-amyl-ol is higher than that of water. This prediction is in good agreement with the results reported by Palacios et al. (1996). These results are useful when selecting a heating media for chemical reactions in the presence of a microwave field.

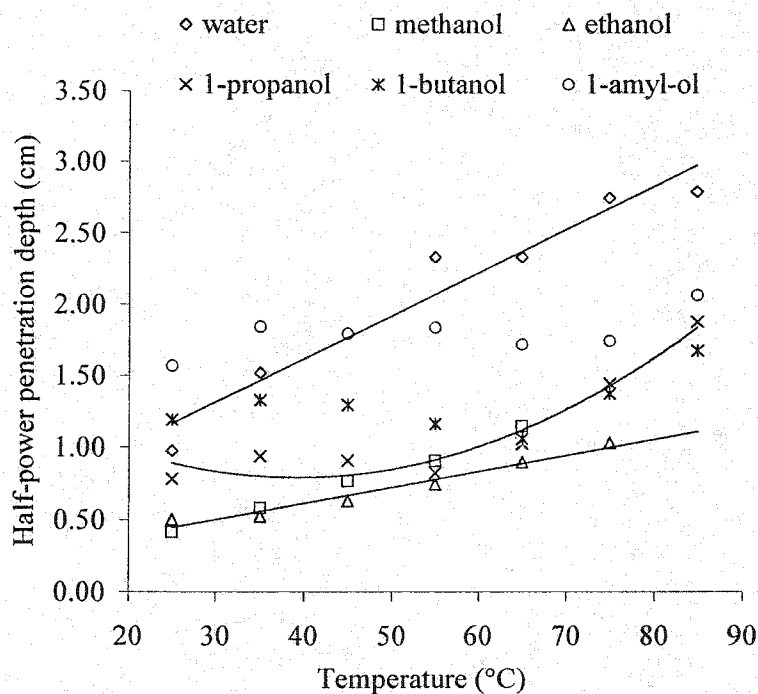


Figure 3.6: Half-power penetration depth of water and alcohols vs temperature at 2450 MHz.

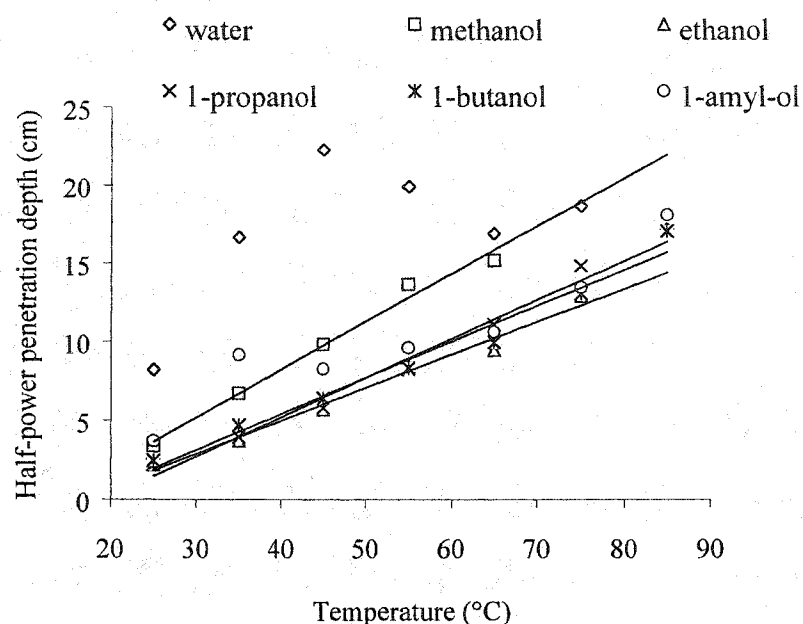


Figure 3.7: Half-power penetration depth of water and alcohols vs temperature at 915 MHz.

In order to describe the relationships between the half-power penetration depth and temperature, both linear ($i = 0$) and quadratic equations ($i \neq 0$) were adopted:

$$d_{\frac{p}{2}} = i * T^2 + g * T + h \quad (3.7)$$

Where, T indicates the temperature in °C which is below the boiling point and the parameters i , g , h in equation (3.7) determined by the least square method are summarized in Table 3.3.

At 2450 MHz, the behavior of half-power penetration depth of both ethanol and water has a good linear relationship with temperature ($i = 0$) (Figure 3.6 and Table 3.3). For 1-propanol, it is better to use the quadratic equation to describe the behavior of half-power penetration depth at different temperatures ($i = 0.005 \neq 0$) (Figure 3.6 and Table 4.3). However, neither linear nor quadratic equations can give the suitable description of the half-power penetration depth at different temperatures for other materials measured. It probably results from the much different responses of molecular structure of alcohols to microwave field. Interestingly, at 915 MHz, the half power-penetration depth of all the alcohols tested except 1-amyl-ol linearly varied with temperature (Figure 3.7). This information can help us to describe the temperature distribution in the microwave-assisted

chemical reaction due to the fact that the microwave-heating rate is linked to the half-power penetration depth of material.

Table 3.3: Regression equation constants and coefficients of determination (r^2) of the equations for the half-power penetration depth for alcohols and water between 25-85 °C at both frequencies.

Alcohol	2450 MHz			Coeff.	915 MHz			Coeff.
	iT ² + gT +h				iT ² + gT +h			
	i	g	H		r ²	i	g	
Methanol	&	&	&		0	0.31 ^{***}	-3.98 ^{**}	0.986
Ethanol	0	0.11 ^{***}	.165 ^{**}	0.965	0	0.21 ^{***}	-3.4 ^{***}	0.984
1-propanol	.0005 ^{***}	-.039	1.56 ^{**}	0.936	0	0.25 ^{***}	-4.7 ^{***}	0.978
1-butanol	&	&	&		0	0.23 ^{***}	-3.7 ^{***}	0.973
1-amyl-ol	&	&	&		&	&	&	
Water	0	0.03 ^{***}	.412 ^{**}	0.945	&	&	&	

***: significant at 0.0001; **: significant at 0.001; *: significant at 0.01.

&: Means that neither linear nor quadratic relationship between the half power penetration depth with temperature was found

3.5 Conclusions

The dielectric constant of all alcohols tested increased with temperature. At both frequencies, the dielectric loss factors of methanol decreased with temperature, while the other alcohols tested, except ethanol, first increased and then decreased with temperature. The half-power penetration depth of water is higher than those of alcohols tested at both frequencies. The information obtained in this work could be useful for chemists and chemical engineers as a guide for the selection of an alcohol as a solvent in a particular microwave-assisted reaction compared with water in terms of microwave heating rate.

Acknowledgments

We thank CIDA (Canadian International Development Agency) and NSERC (National Science and Engineering Research Council of Canada) for financial support.

3.6 References

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CONNECTING TEXT

Results in Chapter III clearly demonstrated functionalities of half-power penetration depth and dielectric properties with temperature. The dielectric constants of all alcohols tested increase with temperature at microwave frequencies of 2450 and 915 MHz, the dielectric loss factors of methanol decrease with temperature, while the other alcohols tested, except ethanol, first increase and then decrease with temperature. The half-power penetration depth of water is higher than those of alcohols tested at both frequencies. It can be used to explain the changes in dielectric properties before reaction and after reaction. Due to the fact that we chose to study Maillard reaction consisting of glucose, lysine and water, we need to know the dielectric properties of aqueous glucose solutions at both frequencies. Furthermore, our preliminary study showed that at 22°C, within a concentration range of 40-60% (w/w) the loss factor of glucose aqueous solutions almost remains constant. It prompted us to investigate the dielectric properties of supersaturated α -D-glucose aqueous solutions at 2450 MHz at varying temperatures. In this Chapter IV, the dielectric properties of α -D-glucose aqueous solutions at 2450 MHz were presented.

The material presented in this chapter has already appeared in a peer reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., Meda, V., and Yaylayan, V. A. 2001. Dielectric properties of supersaturated α -D-glucose aqueous solutions at 2450 MHz. *Journal of Microwave Power & Electromagnetic Energy*, 36 (3): 131-138.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second author is one of the co-supervisors who contributed in all aspects of the project, (iii) the third author provided input in the design aspect of the experimental setup, (iv) the fourth author is a co-supervisor.

IV. DIELECTRIC PROPERTIES OF SUPERSATURATED α -D-GLUCOSE AQUEOUS SOLUTIONS AT 2450 MHz.

4.1 Abstract

Dielectric properties of supersaturated α -D-glucose aqueous solutions (45-56% w/w) at 2450 MHz were investigated at temperatures ranging from 25 to 85°C. Penetration depth was calculated as well. At each temperature tested, there exists a concentration range at which the dielectric constants or loss factors for supersaturated glucose solutions are independent of concentration. These results will be helpful in studies of the Maillard reaction as it occurs in a microwave field.

4.2 Introduction

Microwave energy has been applied in many fields, especially in the food industry and scientific research such as communication, microwave-assisted chemistry (Decareau, 1985). The successful application of microwaves is directly associated with the dielectric properties of the materials. An accurate measurement and working knowledge of these properties are key factors in better understanding the interaction of microwaves with food materials. These properties are defined in terms of dielectric constant (ϵ') and loss factor (ϵ''). The former is a measure of the ability of a material to store electric field energy and the latter is a measure of the ability of a material to dissipate electric energy, converting it into heat. Penetration depth (D_p) shows how far a wave will penetrate before it is reduced to $1/e$ of its intensity at the surface (Mudgett, 1986).

Although many foods can be cooked with microwave energy, products cooked with microwaves often show organoleptic qualities inferior to conventionally cooked foods. This is often attributable to insufficient heating-time for the reactions involved in food color and flavor development to be completed. To improve the quality of microwave-cooked products, a modified product formulation which enhances reactions leading to the desired organoleptic traits, must be determined. Amongst other characteristics, dielectric properties of food components must be considered in

developing such formulations. The Maillard reaction, an extensively studied chemical reaction in food processing and flavor chemistry, has recently been shown to have an important role in fields as diverse as human pathology and flavor chemistry (Ikan, 1996), with far reaching implications in the production of flavors and aromas, nutrition, toxicology, and food processing technology (Yaylayan, 1997). Glucose is frequently one of the primary reducing sugars involved in the Maillard reaction. An early determination at 25°C of the dielectric properties of glucose aqueous solutions (10-70%) at microwave frequencies of 3000 and 1000 MHz showed that the dielectric constants decrease but the loss factors increase with concentration for all solutions studied (Roebuck et al., 1972). However, our preliminary study showed that at 22°C, within a concentration range of 40-60% (w/w) the loss factor of glucose aqueous solutions almost remained constant. The dielectric properties of supersaturated α -D-glucose aqueous solutions at 2450 MHz at temperatures above 22°C are little studied. The lack of consensus or information in these areas led us to investigate the dielectric properties of supersaturated α -D-glucose aqueous solutions at 2450 MHz at varying temperatures. The dielectric behavior of specific solutions exposed to microwaves at different temperatures will allow a better understanding of microwave-assisted Maillard reactions involving glucose (Liao et al., 2000) and more generally the kinetic mechanism of microwave-enhanced chemical reactions.

4.3 Materials & Methods

4.3.1 Aqueous solutions of glucose

Standard glucose aqueous solutions (10-60%) were prepared by placing preweighed amounts of glucose into suitable bottles, which were filled with distilled water to a specified volume. The accuracy of the balance was ± 0.0001 g. The accuracy of the volume determination was ± 0.2 -ml. α -D-glucose (ACS Reagent) was purchased from Aldrich Chemical Company Inc. (USA) and used without further purification. A standard microwave oven was used to aid in the complete dissolution of the glucose. Then, the solution was stirred by magnetic stirrer and naturally cooled to room temperature. To

avoid loss of glucose due to microorganismal activity or precipitation, the measurements started immediately after the sample temperature cooled to room temperature.

4.3.2 Measurement of dielectric properties

Dielectric properties at 2450 MHz were measured by using the cavity perturbation technique, requiring a dielectric analyzer (Meda and Raghavan, 1998), a PC, resonant cavity made of copper (i.d. = 90mm; h = 45mm; TM₀₁₀ simplistic mode), and heating/cooling unit (Isotemp 1013S, Fisher Scientific Inc.) (Figure 4.1). The system was calibrated with distilled water, a liquid of known dielectric properties. The sample was confined in a 10 µl borosilicate glass sample holder (Fisherbrand Micropipet). The circulating fluid, ethylene glycol, transferred heat from coils attached to the external walls of the resonant cavity, thus maintaining the temperature of the cavity and sample at the desired level. Dielectric measurements of all glucose solutions were performed at the specific temperatures discussed. The accuracy for temperature measurement was $\pm 0.1^\circ\text{C}$. The following equations were used to calculate ϵ' and ϵ'' (Meda, 1996):

$$\epsilon' = 1 + 0.539 \left(\frac{V_o}{V_s} \right) (\Delta f) \quad (4.1)$$

$$\epsilon'' = 0.269 \left(\frac{V_o}{V_s} \right) \left(\frac{1}{Q_s} - \frac{1}{Q_o} \right) \quad (4.2)$$

$$\Delta f = \frac{f_o - f_s}{f_s} \quad (4.3)$$

Where: V_s and V_o are the volumes of the sample and the cavity, respectively; f_o and f_s are the resonant frequencies of the empty and sample loaded cavity, respectively; Q_o and Q_s are the quality factors of the empty and sample loaded cavity, respectively.

4.3.3 Statistical analysis

Analysis of variance was used to determine significant differences in ϵ' and ϵ'' among the aqueous solutions of glucose. Three samples were used for each solution. Linear regressions between ϵ' or ϵ'' and either glucose concentration or temperature were obtained using PROC GLM in SAS (Version 6.12 for Windows 98). In this

procedure, the significance of the intercept value and slope were tested. Regressions relating penetration depth to temperature and glucose concentration were obtained for each glucose solution using PROC STEPWISE in SAS (Version 6.12 for Windows 98). Similarly to the linear regressions, the coefficients for the different temperature-concentration terms were tested for their significance.

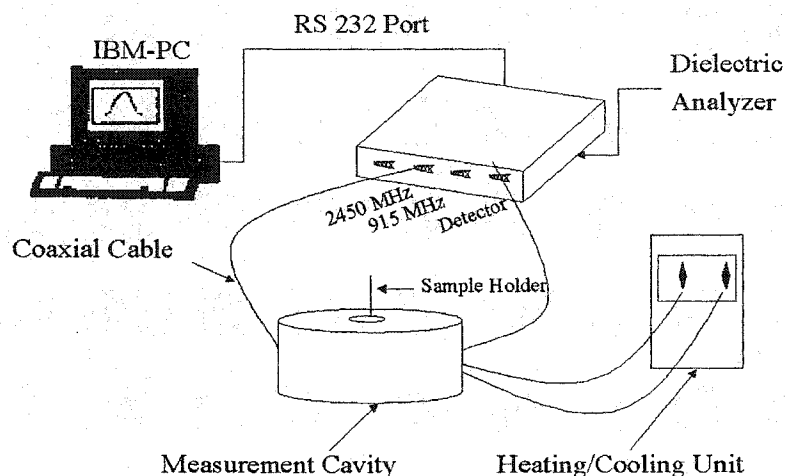


Figure 4.1: Schematic diagram of measurement set-up.

4.4 Results & Discussion

4.4.1 The dielectric constant and loss factor

The dielectric constant (ϵ') and loss factor (ϵ'') of glucose solutions at 22°C as a function of concentration (w/w) are shown in Figure 4.2. This concentration ranges from 10% (diluted solution) to 60% (supersaturated solution). As glucose concentration increases, ϵ' decreases considerably except at concentrations of 45% and 53%. Such short plateaus in the ϵ' -solute concentration relationship have also been observed for carbohydrates (Roebuck et al., 1972), and may be attributable to the exclusion of free water by carbohydrates and stabilization of the hydrogen bonds by the hydroxyl groups. Glucose concentrations of 47% and 56% were tested to validate our hypothesis that at

22°C, for a glucose concentration ranging from 40% to 60%, the ϵ'' value is independent of concentration. Figure 4.2 confirms this hypothesis.

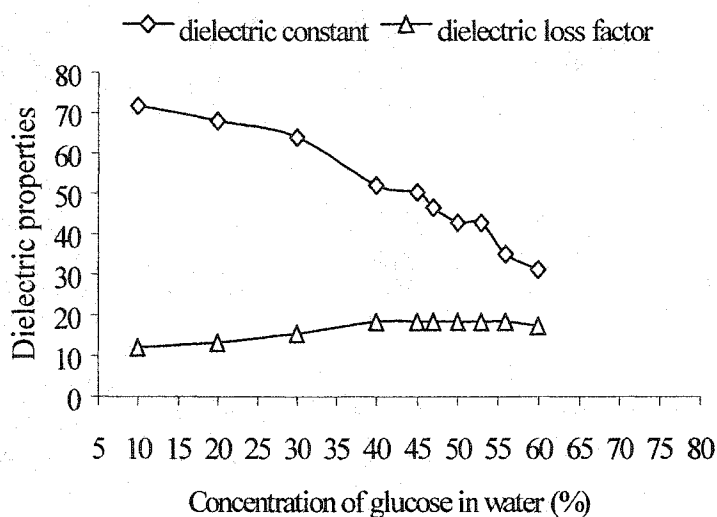


Figure 4.2: Dielectric properties of α -D-glucose solutions in water at 22°C.

The effect of glucose concentration on the ϵ' value at different temperatures is presented in Figure 4.3. The means of three replicates were plotted as there are no significant differences between the replicates. For a given concentration, the ϵ' value increases with temperature. For a given temperature, the ϵ' value generally decreases with an increase in concentration. However, the ϵ' value for a 45% solution is quite close to that of a 47% solution at all temperatures tested. The ϵ' values for both a 52% and 53.12% solutions are also quite close at temperatures varying from 25 to 65°C but differs notably between 75 and 85 °C. At 85°C, ϵ' values are constant for glucose solutions ranging from 45% to 49.5% (Figure 4.3).

The effect of the concentration of glucose solutions at different temperatures on the loss factor, ϵ'' , is presented in Figure 4.4. Unlike the dielectric constant, ϵ'' values decrease with temperature and generally increase with concentration (Figure 4.4). As with the ϵ' , at 85°C, ϵ'' values are constant for glucose solutions ranging from 45 to 49.5% (Figure 4.4). In the glucose concentration range of 45-52%, at 25° two concentrations (47 and 49.5%) showed similar ϵ'' values. Similar values were noticed for three concentrations (45, 47, and 49.5%) at 55°C and for four concentrations (45, 47, 49.5 and

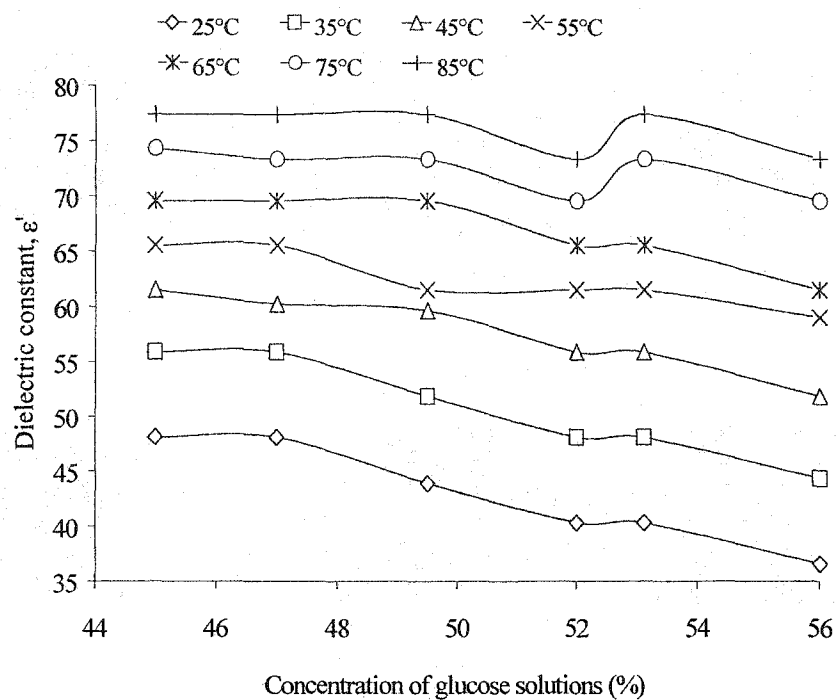


Figure 4.3: Dielectric constant vs concentration of glucose solutions.

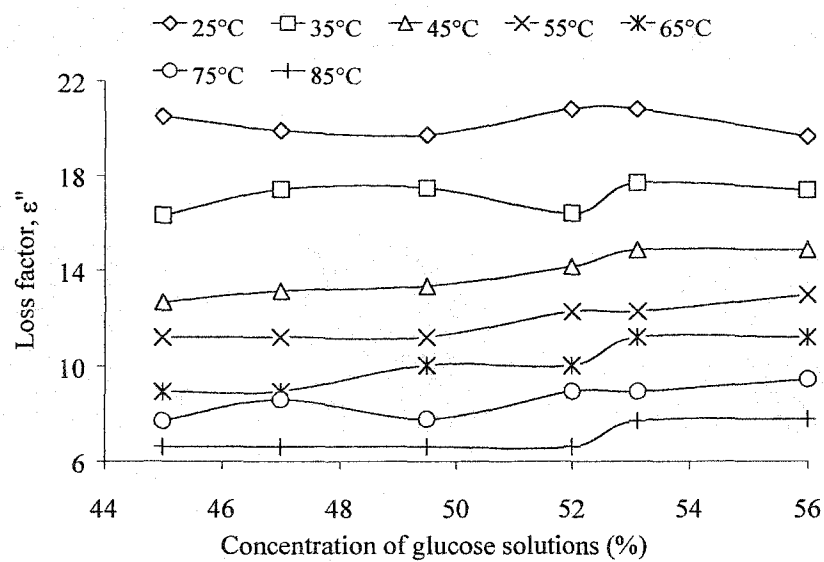


Figure 4.4: Loss factor vs concentration of glucose solutions.

52%) at 85°C (Figure 4.4). This phenomenon probably arises from the decrease in the relative saturation of the solution as the solubility of glucose increases with rising temperatures.

4.4.2 Penetration depth of supersaturated glucose solutions

Penetration depth is an effective and convenient measure to compare the relative microwave absorbing characteristics of materials and to relate the dielectric properties and geometry to microwave heating. Penetration depth for a material was calculated as (Metaxas and Meredith, 1983):

$$D_p = \frac{\lambda_0}{2\pi(2\varepsilon')^{0.5}} \left\{ \left[1 + \left(\frac{\varepsilon''}{\varepsilon'} \right)^2 \right]^{0.5} - 1 \right\}^{-0.5} \quad (4.4)$$

where, D_p is the penetration depth (cm), and λ_0 is the wavelength in free space (12.237cm at 2450 MHz).

Changes in penetration depth of different concentrations of glucose solutions with respect to temperature are presented in Figures 4.5 and 4.6. An increase in temperature resulted in an increase in penetration depth at all concentrations tested. At temperatures

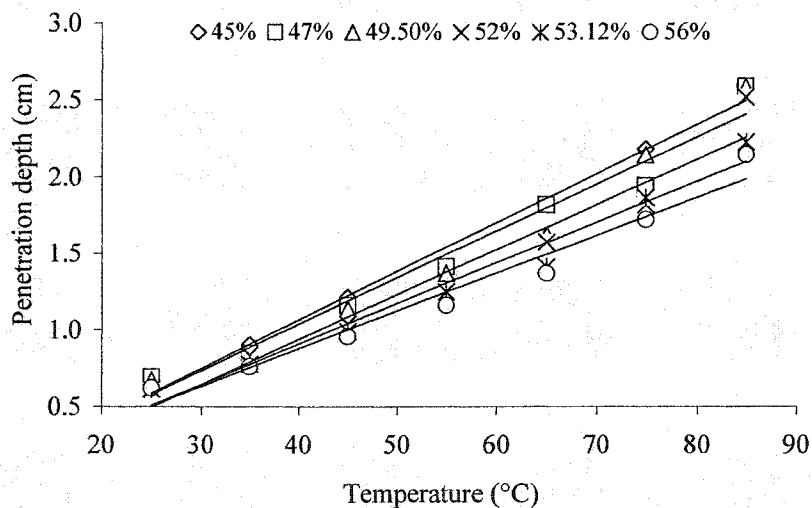


Figure 4.5: Penetration depth vs temperature of glucose solutions.

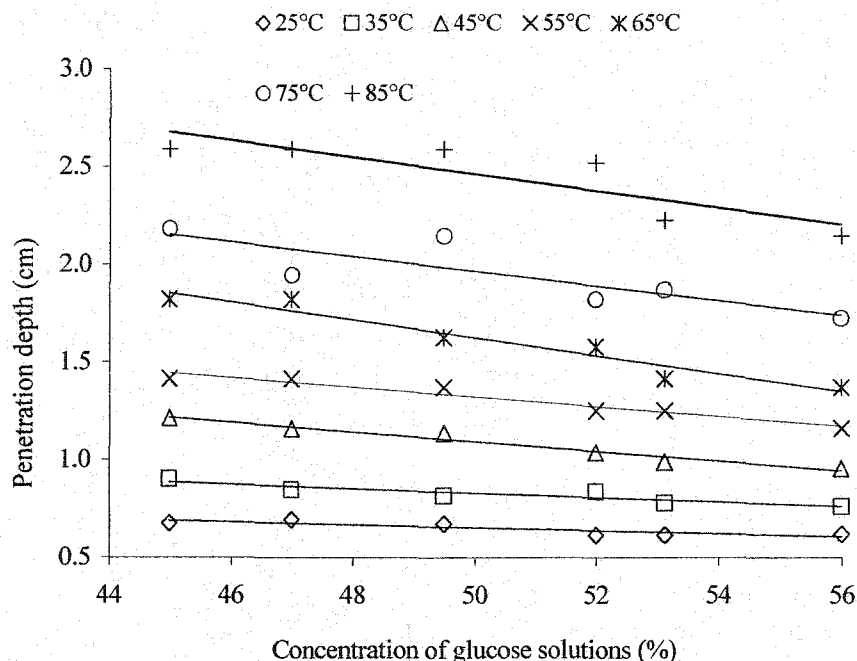


Figure 4.6: Penetration depth vs concentration of glucose solutions.

ranging from 25 to 45°C, the higher the glucose concentration, the shorter is the penetration depth. This was expected, because in the materials with high ϵ'' values, microwave energy does not penetrate very deeply (Decareau, 1985). Shorter penetration depths indicate that the microwave power is absorbed more readily. This result can be useful when selecting a heating media and formulation for chemical reactions in a microwave field. Regression analysis was performed to relate the penetration depth of glucose solutions to temperatures (25~85°C) and concentrations (45~56%) using PROC GLM in SAS. In Figures 4.5 and 4.6, the points represent the calculated penetration depth from experimental data and the lines are curves fitted to the experimental points. For a given concentration, the variation in D_p with temperature (°C) is found to be linear and significant except the intercept value (A_1) (Figure 4.5). The regression lines for 47 and 49.5% are almost the same (Figure 4.5). Linear regression constants and coefficient of determination (R^2) of D_p vs. temperature for each glucose concentration are presented in Table 4.1. The variation in D_p with concentration was also found to be linear and

significant (Figure 4.6). The results of linear regressions at each temperature studied are given in Table 4.2.

Table 4.1: Coefficients for the linear regression of penetration depth of supersaturated glucose solutions with temperature.

$$(D_p = b_1 T + A_1)$$

Concentration (%)	b_1	A_1	R^2
45	0.03185	-.209556	0.9880
47	0.03053	-.183969	0.9699
49.5	0.03183	-.272107	0.9692
52	0.02941	-.238344	0.9479
53.12	0.02661	-.158156	0.9716
56	0.02473	-.112294	0.9642

Table 4.2: Coefficients for the linear regression of penetration depth of supersaturated glucose solutions with concentration.

$$(D_p = b_2 c + A_2)$$

Temperature (°C)	b_2	A_2	R^2
25	-.74831	1.024476	0.7218
35	-1.15961	1.407545	0.8403
45	-2.48313	2.333537	0.9653
55	-2.48543	2.563333	0.9398
65	-4.57762	3.912973	0.9351
75	-3.75906	3.843569	0.6963
85	-4.28196	4.604128	0.7389

4.4.3 Predictive model for penetration depth of supersaturated glucose solutions

The following model for D_p as a function of concentration (c) and temperature (T) was developed with a PROC STEPWISE analysis in SAS:

$$D_p = 0.00026T^2 - 0.05219cT + 0.02716T + 0.48006 \quad (4.5)$$

$$(R^2 = 0.9884, P \leq 0.0001)$$

where, T = temperature, $25 \leq T \leq 85$ °C, and c = concentration of glucose solutions, $45\% \leq c \leq 56\%$

The model can be used to determine the penetration depth of supersaturated glucose solutions at given concentrations and temperatures.

4.5 Conclusions

The dielectric constant of supersaturated α -D-glucose solutions at 2450 MHz increased with temperature, but generally decreased with concentration. The dielectric loss factor decreased with temperature, but generally increased slightly with concentration. At temperatures tested, at least two concentrations showed nearly identical values of dielectric constant or dielectric loss factor. Further studies at other microwave frequencies such as 915 MHz and under different temperature ranges are needed to fully justify the findings of this study and shed some light on microwave-assisted chemical reactions and food processing. Variation in penetration depth was found to vary linearly with concentration or temperature, increasing with temperature and decreasing with concentration. A predictive model was developed to calculate penetration depth for a supersaturated glucose solution as a function of both concentration and temperature. Such a model could be applied to predict microwave-heating patterns in chemical reactions involving glucose and water.

Acknowledgments

We thank CIDA (Canadian International Development Agency) and NSERC (National Science and Engineering Research Council of Canada) for financial support.

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CONNECTING TEXT

Results in Chapter IV clearly demonstrated that the dielectric constant of super-saturated α -D-glucose solutions at 2450 MHz increased with temperature, but generally decreased with concentration. The dielectric loss factor decreased with temperature, but generally increased slightly with concentration. At each temperature tested, at least two concentrations showed nearly identical values of dielectric constant or dielectric loss factor. Due to the solubility of glucose in water, generally, in the Maillard reaction model system, a lower concentration is chosen as a subject. Therefore, it encouraged us to investigate the dielectric properties for the other concentration at 2450 MHz, especially in lower concentrations.

The material presented in this chapter is being evaluated by a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2001. Dielectric properties of α -D-glucose aqueous solutions at 2450 MHz. *Food Research International*.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

V. DIELECTRIC PROPERTIES OF α -D-GLUCOSE AQUEOUS SOLUTIONS AT 2450 MHz

5.1 Abstract

Dielectric properties of α -D-glucose aqueous solutions at 2450 MHz were measured at concentrations varying from 10 to 60% (weight percent) at temperatures ranging from 0-70°C using a cavity perturbation technique. Dielectric constant increased with temperature but decreased with concentration. Loss factor decreased with temperature but increased with concentration (10-56%) in the temperature range of 30-70°C. Dielectric constants for higher concentration glucose solutions were more influenced by higher temperatures than at lower temperatures. Loss factors for higher concentration glucose solutions were less influenced by higher temperatures than at lower temperatures. Using PROC STEPWISE in SAS generated predictive models of the dielectric properties as functions of concentration and temperature. The results are useful in estimating the volumetric heating of these solutions by microwave energy, studying the dielectric behavior of the glucose solutions, and chemical reactions such as Maillard reaction, mutarotation involving glucose aqueous solutions in a microwave field.

5.2 Introduction

The successful use of microwave is directly associated with the dielectric properties of the material. Dielectric properties are key factors in better understanding of interactions of microwaves with food materials. Dielectric properties of materials are defined in terms of dielectric constant (ϵ') and loss factor (ϵ''). ϵ' is a measure of the ability of a material to couple with microwave energy and ϵ'' is a measure of the ability of a material to heat by absorbing microwave energy (Mudgett, 1986). Although many foods can be heated by microwave energy, less satisfactory products are obtained in the microwave oven. This is attributed to the short heating time that is insufficient to complete the reactions involving the formation of food color and flavor. In order to improve the quality of a product in a microwave field, it is necessary to use a suitable

formulation that can enhance the desired reactions to produce the desirable color and flavor. Dielectric properties of materials, to some degree, will give an idea which formulation will be heated in a microwave field since microwave heating is directly linked to dielectric properties of materials. The Maillard reaction is a typical chemical reaction in food processing and flavor chemistry. It has far reaching implications in the production of flavors and aromas, nutrition, toxicology, human pathology, technology of food processing (Ikan, 1996; Yaylayan, 1997). Glucose is an important reducing sugar in the Maillard reaction. Its water solution has peculiar optical activity (Volodymyr, 1996). Many investigations on the dielectric properties of glucose aqueous solutions exist, but none of them have focused on microwave frequency of 2450 MHz and different temperatures. Roebuck et al., (1972) reported the dielectric properties of glucose aqueous solutions at 25°C at microwave frequencies of 3000 and 1000 MHz. Some studies about dielectric relaxation of the glucose solutions to explain and determine the motion or structure of molecules in solutions were reported (Suggett, 1976; Chan et al., 1986; Mashimo et al., 1992; Noel et al., 1996; Moran et al., 2000). In addition, the use of dielectric properties of glucose solutions to elucidate the behavior and molecular dynamics has been recently reported by others (Hochtl et al., 2000; Fuchs and Kaatz, 2001). However, these dielectric properties do not allow the study of the underlying mechanisms of microwave-assisted chemical reactions involving glucose solutions. The misconception that materials possessing higher dielectric constants heat rapidly while those with lower dielectric constants heat slowly under microwave has misled many people in their selection of heating media for chemical reaction or extraction in a microwave field. When a material absorbs microwaves at 2450 or 915 MHz, the temperature profile for the material is dependent on both the dielectric constant and loss factor at these frequencies, not only on those dielectric constants mentioned in the literature, which are actually static permittivities or at other frequencies. As different types of glucose solutions differentially affect the heating characteristics of material during microwave heating, the selection of solutions is the most influential factor on the heating rate of microwave-assisted chemical reactions. However, data about the dielectric properties of α -D-glucose aqueous solutions at 2450 MHz at elevated temperatures are rare or non-existent. Furthermore, there are no reports about the relationships (models) between the dielectric properties of α -D-glucose aqueous solutions, the temperatures and

their concentrations. Both prompted us to investigate the dielectric properties of α -D-glucose aqueous solutions at 2450 MHz at varying temperatures. The dielectric properties of these specific solutions will not only be useful for microwave-assisted Maillard reaction involving glucose (Liao et al., 2000), but also can help understand the mechanisms of microwave-enhanced chemical reactions and the mutarotation of the glucose solutions (Pagnotta et al., 1993).

5.3 Materials & Methods

5.3.1 Materials

α -D-glucose was purchased from Aldrich Chemical Company, Inc. (USA) and was used without further purification.

5.3.2 Glucose aqueous solutions

The solutions were prepared by adding amounts of glucose into suitable bottles, which were filled with distilled water to the specific volumes. Microwave heating was employed to make them dissolve completely. In order to avoid any effects from disintegration of glucose by microorganisms and precipitation, the measurement started as soon as the temperature of sample was cooled closer to 0°C.

5.3.3 Dielectric properties measurement

Each sample solution was confined in a 10- μ l sample holder (Borosilicate glass Fisherbrand Micropipets). As soon as the temperature reached 0°C, the first measurement of dielectric properties was made. A heating/cooling unit facilitated heating of the sample to 10°C. On attaining this temperature, a second measurement of dielectric properties was made. This procedure was repeated for temperatures of 20, 30, 40, 50, 60, 70°C. Three replicates were performed for each sample.

Dielectric properties were measured by using a cavity perturbation technique at 2450 MHz. The measurement required a dielectric analyzer (Gautel Inc.), a PC, measurement cavity, and heating/cooling unit. The system software calculated the dielectric parameters from the cavity Q factor, transmission factor (ΔT), and the shift of

resonant frequency (ΔF). Details about measurement and theoretical background have been reported in Chapter III (Liao et al., 2001). Before starting measurements, the calibration was verified by taking measurements on a standard liquid (water) with known dielectric properties.

5.3.4 Statistical analysis

Analysis of variance was used to determine differences among the glucose aqueous solutions. Regressions obtained for each solution were used to relate dielectric properties to temperature and concentration using PROC GLM and PROC STEPWISE in SAS (Version 6.12 for Windows 98).

5.4 Results & Discussion

Dielectric properties of glucose solutions were shown to be dependent on the concentration and temperature (Tables 5.1 and 5.2).

5.4.1 Effect of concentration and temperature on dielectric constant of glucose solutions

For a given concentration, the dielectric constant increases with temperature. A representative figure of this observation is given by 10% and 50% of glucose solutions (Figure 5.1). 10% glucose solution has the highest dielectric constant among the solutions tested at varying temperatures. As the temperature increases, the value difference of dielectric constant for the different concentrations becomes smaller and smaller. For example, when temperature is 0°C, the value difference between 10% and 50% is more than 40, while when temperatures reaches 70°C, the difference is less than 16. It means that dielectric constant for higher concentration solutions were more influenced by higher temperature than lower one. As for a given concentration, the variation in ϵ' with temperature (°C) was found to be quadratic and significant at 0.001 level. The constants of the regression lines for each concentration are given in Table 5.3 along with resulting

Table 5.1: The effects of temperature on dielectric constant of different concentrations of glucose aqueous solutions.

Temp.(°C) ^a	Concentration (%)							
	10	20	30	40	45	50	56	60
0	73.85	63.64	54.80	39.52	37.92	30.42	22.92	19.44
10	80.02	73.85	66.33	50.78	50.78	43.28	35.51	31.76
20	83.87	80.02	73.85	62.31	58.55	50.78	43.28	39.52
30	87.81	83.78	76.99	70.09	66.33	62.31	54.80	50.78
40	87.81	83.78	80.02	71.97	70.09	66.33	58.50	54.80
50	91.84	87.81	83.87	75.99	75.99	71.97	66.33	62.31
60	91.84	87.81	87.81	80.02	80.02	75.99	71.97	68.21
70	95.60	91.84	91.84	83.78	83.78	80.02	75.99	75.99

^a: Temp.: temperature in °C. (Each measurement is mean of three replications)

Table 5.2: The effects of temperature on dielectric loss factor of different concentrations of glucose aqueous solutions.

Temp.(°C) ^a	Concentration (%)							
	10	20	30	40	45	50	56	60
0	26.64	29.62	31.38	29.55	27.30	23.01	18.65	16.49
10	18.68	21.47	23.64	25.89	24.80	22.91	19.19	17.04
20	14.19	15.27	17.60	21.47	21.47	20.39	19.22	17.04
30	10.77	11.85	13.61	17.06	17.04	17.04	17.55	14.87
40	8.44	9.60	11.08	13.01	13.63	14.79	15.97	13.70
50	7.35	8.44	9.60	10.77	11.92	11.85	13.72	13.70
60	6.19	6.19	7.27	8.88	9.60	10.77	11.85	11.85
70	5.10	6.19	7.35	8.44	8.44	8.52	10.19	10.77

^a: Temp.: temperature in °C. (Each measurement is mean of three replications)

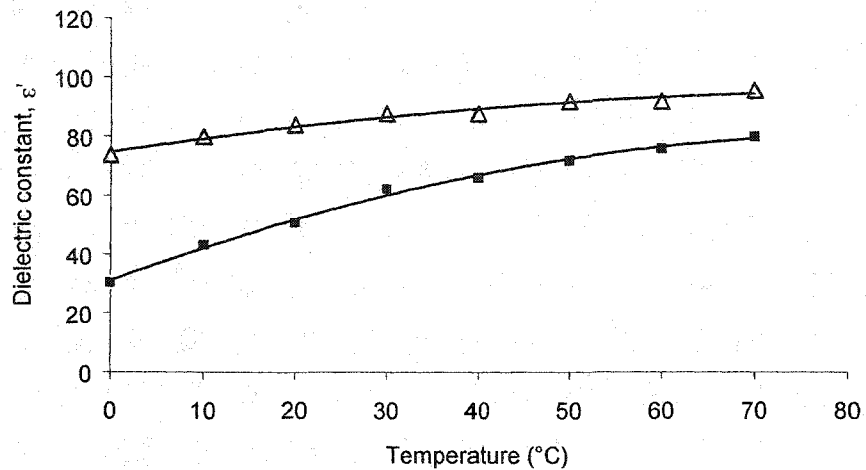


Figure 5.1: Variation of dielectric constant of glucose solutions at different temperatures
 (Δ): 10%; (\blacksquare): 50%.

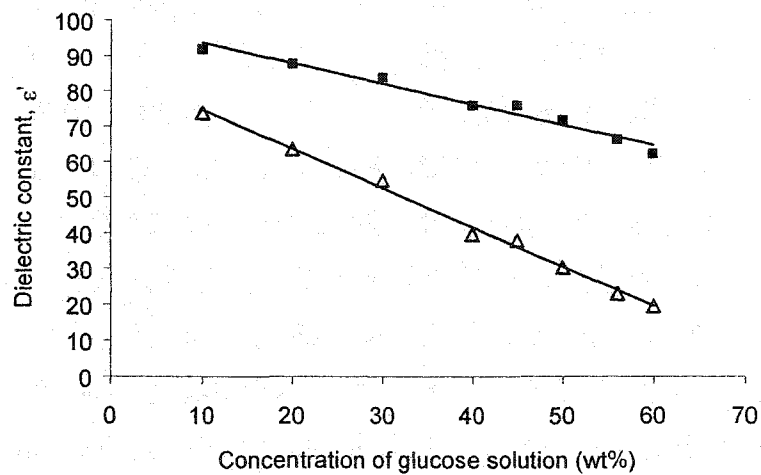


Figure 5.2: Variation of dielectric constant of glucose solutions at different concentrations
 (Δ): 0°C; (\blacksquare): 50°C.

R^2 (coefficient of determination) values. At 0, 20, 30, and 40°C, the dielectric constant decreased with an increase in concentration. At other temperatures, it generally decreased with concentration. A representative figure of this is given for the glucose solution at 0°C and 50°C (Figure 5.2). The observations are similar to reports on carbohydrate (Roebuck, et al., 1972), and may be attributed to the exclusion of free water by carbohydrates and stabilization of the hydrogen bonds by the hydroxyl groups. Variation of ϵ' at a given temperature is linear and significant at 0.0001 level with a coefficient of variation (CV) between 2 and 5%. The results of linear regressions at each temperature studied are given in Table 5.4. The slope of the regression line increases with temperature. It means that dielectric constant at lower temperature is more influenced by concentration than that at higher temperature.

5.4.2 Effect of concentration and temperature on loss factor of glucose solutions

For a given concentration, the loss factor decreased with temperature. A representative figure for 10% and 50% of glucose solutions is shown in Figure 5.3. At a given temperature, functionality of loss factor with concentration is not always the same. When temperature is below 30°C, the loss factor first increases with concentration and then decreases with concentration, while when temperature is higher than 40°C, the loss factor increases with concentration (10-56%). A representative figure of this observation is given at 0°C and 50°C (Figure 5.4). These results may be attributed to the structural changes from mutarotation in molecules (molecule level) of the glucose solutions. Mutarotation is a complicated process influenced by concentration and temperature. The changes in the structure of material will definitely results in the changes in loss factor. Both the variation of ϵ'' with temperature for 50, 56, 60% concentration and the variation of ϵ'' with concentration for 50, 60, 70°C were found to be linear and significant at 0.0001 and 0.004 levels, respectively. The coefficient of variation (CV) was in the range of 5 and 7%. As for as the variation of ϵ'' with temperature for other concentrations and the variation of ϵ'' with concentration for other temperatures are concerned, quadratic relations were suitable and significant at 0.001 and 0.027 levels, respectively. The results of regression lines are given in Tables 5.3 and 5.4.

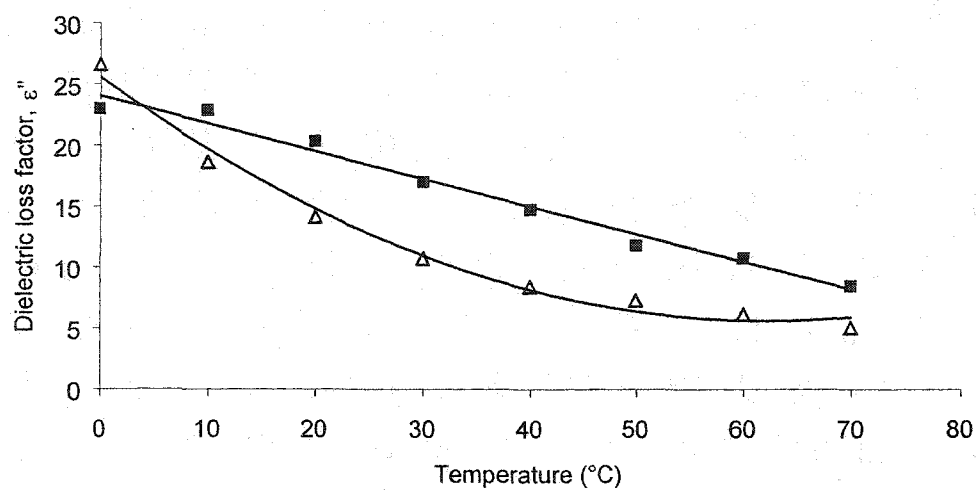


Figure 5.3: Variation of dielectric loss factor of glucose solutions at different temperatures
 (Δ): 10%; (■): 50%.

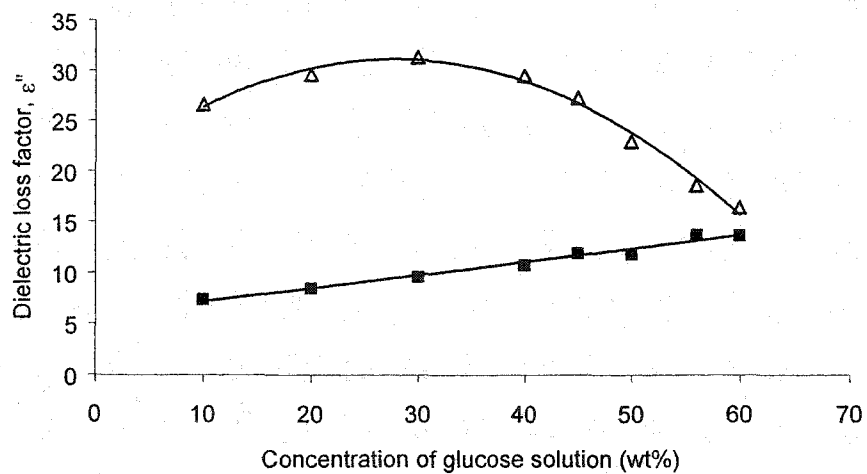


Figure 5.4: Variation of dielectric loss factor of glucose solutions at different concentrations
 (Δ): 0°C; (■): 50°C.

Table 5.3: Regression equation constants and coefficients of equations for different concentrations (x) of glucose aqueous solutions between temperatures (T) 0-70 °C.

Con. ^a	Dielectric constant			R ²	Loss factor			R ²
	A ₁	B ₁	C ₁		A ₂	B ₂	C ₂	
	A ₁ T ² + B ₁ T+C ₁				A ₂ T ² + B ₂ T + C ₂			
10	-0.0028	0.4768	74.81	0.9732	0.0051	-0.6409	25.604	0.9881
20	-0.0054	0.7262	65.656	0.9576	0.006	-0.7298	28.709	0.9891
30	-0.0046	0.7992	57.049	0.9774	0.0058	-0.7336	30.76	0.9945
40	-0.0070	1.1411	40.547	0.9865	0.0032	-0.5437	30.328	0.9942
45	-0.0061	1.0522	39.336	0.9946	0.0019	-0.4154	28.076	0.9918
50	-0.0071	1.1847	31.077	0.9956	0	-0.2262	24.076	0.9811
56	-0.0057	1.1438	23.574	0.9960	0	-0.1358	20.543	0.9015
60	-0.0039	1.0469	20.522	0.9947	0	-0.0918	17.646	0.9051

^a: Con.: Concentration of glucose solution (wt%).

Table 5.4: Regression equation constants and coefficients of equations for different temperatures (T) of glucose aqueous solutions between concentrations (x) 10-60% (wt%).

Temp. ^a	Dielectric constant			R ²	Dielectric loss factor			R ²
	a ₁	b ₁	c ₁		a ₂	b ₂	c ₂	
	a ₁ x ² + b ₁ x + c ₁				a ₂ x ² + b ₂ x + c ₂			
0	0	-110.63	85.82	0.9947	-150	83.43	19.561	0.9861
10	0	-99.71	92.80	0.9831	-121	83.98	10.600	0.9108
20	0	-92.95	97.66	0.9692	-69	59.10	7.742	0.7959
30	0	-74.19	97.95	0.9773	-40	41.07	6.254	0.8442
40	0	-65.38	97.08	0.9607	-13	23.05	5.867	0.9081
50	0	-57.57	99.39	0.9707	0	13.92	5.823	0.8929
60	0	-45.58	98.18	0.9397	0	12.97	4.031	0.9502
70	0	-41.68	101.1	0.9525	0	10.52	4.030	0.9589

^a: Temp.: temperature in °C.

5.4.3 Predictive models for dielectric properties of glucose solutions

In order to develop a model to explain ϵ' and ϵ'' as functions of concentration (x) and temperature (T), the data were analyzed using PROC STEPWISE in SAS. The resulting regression models for ϵ' and ϵ'' are given below:

$$\epsilon' = -0.0054T^2 + 1.03Tx - 64.50x^2 + 0.54T - 64.08x + 80.48 \quad (5.1)$$

$$\epsilon'' = 0.0024T^2 + 0.37Tx - 45.71x^2 - 0.56T + 25.49x + 23.70 \quad (5.2)$$

Where, T = temperature, $0 \leq T \leq 70$ °C, and x = concentration of glucose solutions, $10\% \leq x \leq 60\%$.

The model for ϵ' (Equation 5.1) yielded a coefficient of determination (R^2 value) of 0.9907 and was very significant at the 0.0001 level. The model for ϵ'' (Equation 5.2) gave an R^2 value of 0.9008 and was also significant at the 0.0001 level. Both models could be directly used to compute the values of dielectric properties of glucose solutions at varying concentrations and temperatures.

5.5 Conclusions

Dielectric properties of α -D-glucose solution were shown to be dependent on the temperature and concentration. The dielectric constant generally increased with an increase temperature but generally decreased with concentration. The corresponding loss factors decreased with temperature. When temperature was below 30°C, the loss factor first increased with concentration and then decreased; while when temperature was higher than 40°C, the loss factor increased with concentration. Further study has to be done at other microwave frequencies such as 915 MHz and temperature ranges to fully justify the findings of this study and shed some lights on the microwave assisted chemical reaction, food processing and mutarotation of glucose solutions. Predictive models were developed to obtain dielectric properties for glucose solutions as functions of both concentration and temperature. These models could be applied to predict microwave-heating pattern of chemical reactions involving glucose and water.

Acknowledgments

We thank CIDA (Canadian International Development Agency) and NSERC (National Science Engineering Research Council of Canada) for supporting this research financially.

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CONNECTING TEXT

Results in Chapters IV and V have clearly demonstrated the relationship between the dielectric properties of α -D-glucose solutions at 2450 MHz and temperature or concentration. Microwave frequencies of 2450 and 915 MHz are commonly used in industry. Therefore, it is essential to study the functionalities of dielectric properties of α -D-glucose solutions at 915 MHz. This assists in establishing optimum operating conditions at 915 MHz.

The material presented in this chapter has been accepted for publication in a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2002. Dielectric properties of α -D-glucose aqueous solutions at 915 MHz. *Journal of molecular liquids*. (in press)

The contributions made by different authors are as follows: (i) the first author is the Ph. D student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

VI. DIELECTRIC PROPERTIES OF α -D-GLUCOSE AQUEOUS SOLUTIONS AT 915 MHz

6.1 Abstract

Using a cavity perturbation technique, dielectric properties of aqueous solutions of α -D-glucose at 915 MHz were investigated at concentrations varying from 10 to 70% (w/w) and temperatures ranging between 25-85°C. The dielectric constant increased with temperature but decreased with concentration, whereas the loss factor did the inverse. Dielectric properties of glucose solutions having higher concentration showed greater variation at higher temperatures. Predictive models of the dielectric properties as a function of concentration and temperature were developed by stepwise regression. Such models are useful in estimating the volumetric heating of these solutions by microwave energy, studying the dielectric behavior of the glucose solutions, and chemical reactions involving glucose in aqueous solutions in a microwave field.

6.2 Introduction

Microwave energy has many applications in food industry and scientific research (Decareau, 1985). Microwave allows rapid heating compared to traditional heating methods. The efficiency of microwave heating is directly linked to the dielectric properties of the materials to be heated. Dielectric properties of materials are defined in terms of dielectric constant (ϵ') and loss factor (ϵ''). The former, ϵ' , is a measure of the material's ability to couple with microwave energy and the latter, ϵ'' , is a measure of the material's ability to heat by absorbing microwave energy (Mudgett, 1986). Glucose is one of the important reducing sugars in the Maillard reaction in food chemistry and its aqueous solution has unusual optical activity (Volodymyr, 1996). The dielectric properties of aqueous solutions of glucose have been extensively characterized. Roebuck et al. (1972), for example, reported the dielectric properties of aqueous solutions of glucose at 25°C at microwave frequencies of 3000 and 1000 MHz. The focus of these studies has ranged from the following aspects:

- (i) The use of primary and secondary dielectric relaxation to explain the motion or structure of water molecules in solutions.

Chan et al. (1986) investigated the permittivity and loss factor of glucose in water at 77-350 K in both the glassy and liquid states at $1-10^5$ Hz and observed two relaxation regions, which are above and below the glass transition temperature (T_g). Noel et al. (1996) also studied the dielectric relaxation behavior of a solution of glucose in water with concentrations up to 12.0% (w/w) in the frequency ranging between 10^2 to 10^5 Hz and also found that the primary relaxation was at temperatures which is above T_g and a secondary relaxation at sub- T_g temperatures. The primary relaxations will shift to lower temperatures with the decrease in concentration. Moran et al. (2000) examined the dielectric relaxation data for 40% (w/w) and 75% (w/w) glucose water mixtures in the frequency range between 5 and 13 MHz at temperatures ranging from above room temperature to below the glass transition temperature.

- (ii) The static permittivity (ϵ_0) or the limiting high frequency permittivity (ϵ_∞) (Saito et al., 1997).
- (iii) Dielectric properties to elucidate the behavior and molecular dynamics of glucose in aqueous solution.

Hochtl et al. (2000) used molecular dynamics (MD) trajectories to calculate the static and frequency-dependent dielectric properties of aqueous glucose solutions at least 5 ns length and analyzed the contributions for the dielectric properties from the solute, the solvent, and the solute-solvent cross term. Fuchs and Kaatz (2001) studied the relationship between dielectric relaxation of glucose solutions with their concentrations and the frequency range between 300 kHz and 40 GHz from the point of view of molecular dynamics level. However, none of these studies have focused on a microwave frequency of 915 MHz applied over different temperatures and a mere knowledge of these dielectric properties does not allow the selection of solvents or the study of the underlying mechanisms of microwave-assisted chemistry. The misconception that solvents possessing higher dielectric constants heat rapidly while those with lower dielectric constants heat slowly under microwave irradiation has misled many people in their selection of heating media for chemical reaction or extraction in a microwave field (Liao et al., 2001). When a material absorbs microwaves at 2450 or 915 MHz, the temperature profile of the material depends on both its dielectric constant and dielectric

loss factor at these frequencies, not mainly on the static permittivities presented in the literature. As glucose solutions of varying concentration or composition heat differently under microwave irradiation, the selection of a specific solution is the most influential factor in the heating rate of microwave-assisted chemical reactions involving glucose. Determinations of the dielectric properties of aqueous solutions of α -D-glucose at elevated temperatures at 915 MHz are rare or non-existent. Similarly, models relating the dielectric properties of aqueous solutions of α -D-glucose and solution temperature and concentration have not been developed. The dielectric behavior of glucose solutions of different concentrations when exposed to microwave at different temperatures would not only be useful in the understanding of microwave-assisted Maillard reactions involving glucose (Yaylayan, 1996), but also aid in our understanding of the mechanism of mutarotation and microwave-enhanced chemical reactions, specially, Pagnotta et al. (1993) have observed that in microwave-heated solutions (50 % ethanol-water) of α -D-glucose the ratio of the two anomers of the sugar reaches equilibrium at a faster rate compared to conventional heating and then rises unexpectedly with continued heating under microwave irradiation.

Consequently our objective in this study is to measure dielectric properties of α -D-glucose aqueous solutions at 915 MHz at different temperatures and then create a model relating the dielectric properties to glucose concentration and temperature.

6.3 Materials & Methods

6.3.1 Materials

α -D-Glucose (Analytical Reagent) was purchased from Aldrich Chemical Company Inc. (USA) and was used without further purification.

6.3.2 α -D-Glucose aqueous solutions

The solutions of 10 ~ 70% were prepared by adding appropriate quantities of α -D-glucose into volumetric flasks and filling them to their specific volumes with double distilled water. Microwave heating was employed to aid the dissolution of glucose in

water. In order to avoid losses of α -D-glucose by microorganisms or precipitation, measurement began as soon as the sample temperature dropped to 25°C.

6.3.3 Dielectric properties measurement

Each sample or standard solution was placed in a 10- μ l sample holder (Borosilicate glass Fisherbrand Micropipets) and quickly heated to a specific temperature in a cavity monitored by heating/cooling unit (Isotemp 1013S, Fisher Scientific Inc.) (Figure 6.1). As soon as the temperature reached 25°C, the first measurement of dielectric properties was made. The heating/cooling unit was then allowed to heat the sample to 35°C, at which temperature a second measurement of dielectric properties was made. This procedure was repeated for temperatures of 45, 55, 65, 75, 85°C. Care was taken to ensure proper contact between the bottom of cavity and the sample holder. Six replicates were performed for each sample.

Using a cavity perturbation technique, the dielectric properties of the solutions were measured at 915 MHz. The measurement required a dielectric analyzer (Gautel Inc.), a PC, resonant cavity made of copper (i.d. = 235mm; h = 45mm; TM₀₁₀ simplistic mode), and heating/cooling unit (Isotemp 1013S, Fisher Scientific Inc.) (Figure 6.1). The

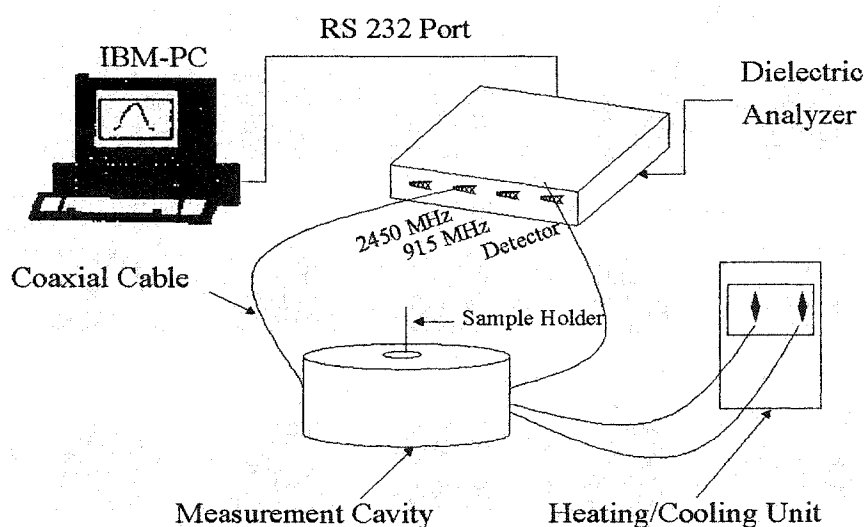


Figure 6.1: Dielectric properties measurement set-up.

system software calculated the dielectric parameters from the cavity Q factor, transmission factor (ΔT) (the changes in the cavity transmission), and the shift of resonant frequency (ΔF). Details about theoretical measurement background have been reported in earlier chapter. Before starting measurements, the calibration was verified by taking measurements on standard liquid (water) of known dielectric properties.

6.3.4 Statistical analysis

Analysis of variance was used to determine differences among the glucose aqueous solutions. Regressions obtained for each solution were used to relate dielectric properties to temperature and concentration using PROC GLM and PROC STEPWISE in SAS (Version 6.12 for Windows 98).

6.4 Results & Discussion

6.4.1 Effect of concentration and temperature on dielectric constant of α -D-glucose solutions

For a given concentration, the dielectric constant increased with temperature (Figure 6.2). The higher temperature is linked to more free water molecules thus resulting in higher dielectric constant. However, as temperature increased, the difference in value of dielectric constants for the different glucose concentrations decreased. For example, at 25°C, the difference in value of ϵ' between 10% and 50% glucose solutions was over 20, whereas at 85°C the difference was less than 10. For a given concentration, the variation in ϵ' with temperature was found to be linear and highly significant. Linear regression constants and coefficient of determination (R^2) of ϵ' vs. temperature relationships for each glucose concentration are presented in Table 6.1. For a given temperature, the dielectric constant decreased with concentration except for 20 and 30% solutions at 45°C (Figure 6.3). The variation in ϵ' with concentration for each given temperature was also found to be linear and highly significant (Table 6.2). Observations at 25°C are similar to those reported by Roebuck et al., (1972) and may be attributed to the exclusion of free water by carbohydrates and stabilization of the hydrogen bonds by the hydroxyl groups. The lower concentration has more free water molecules thus resulting in higher dielectric constant.

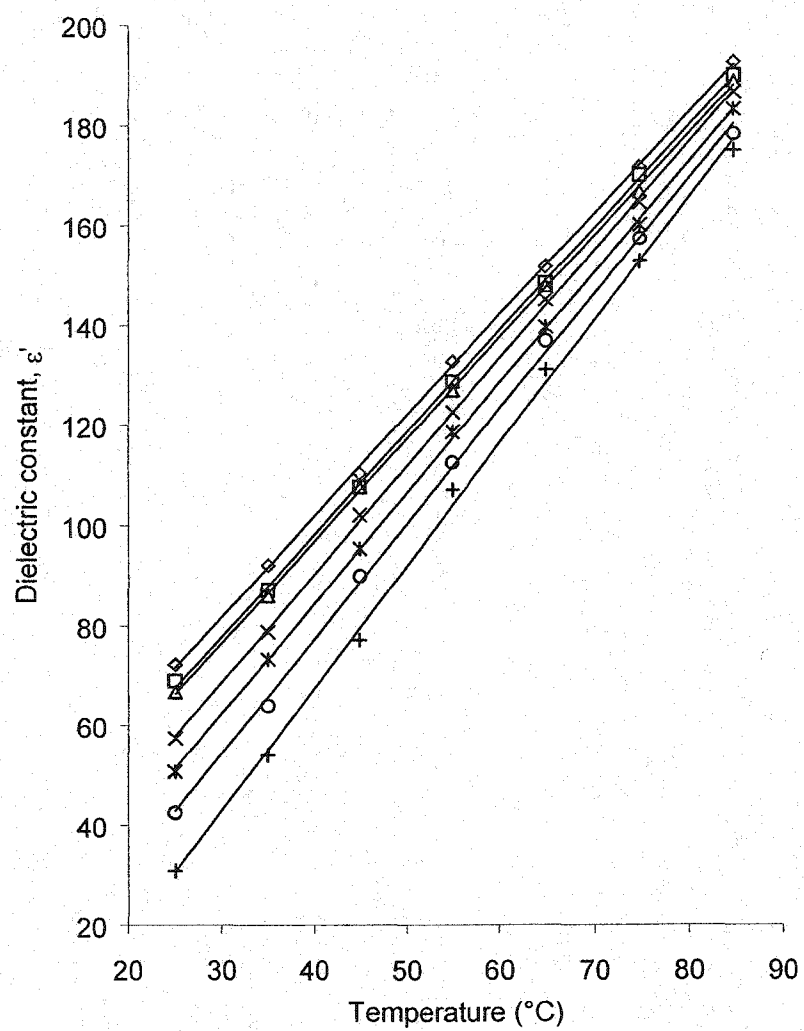


Figure 6.2: Dielectric constant vs temperature of α -D-glucose solutions (◇): 10%; (□): 20%; (Δ): 30%; (×): 40%; (*): 50%; (0): 60%; (+): 70%.

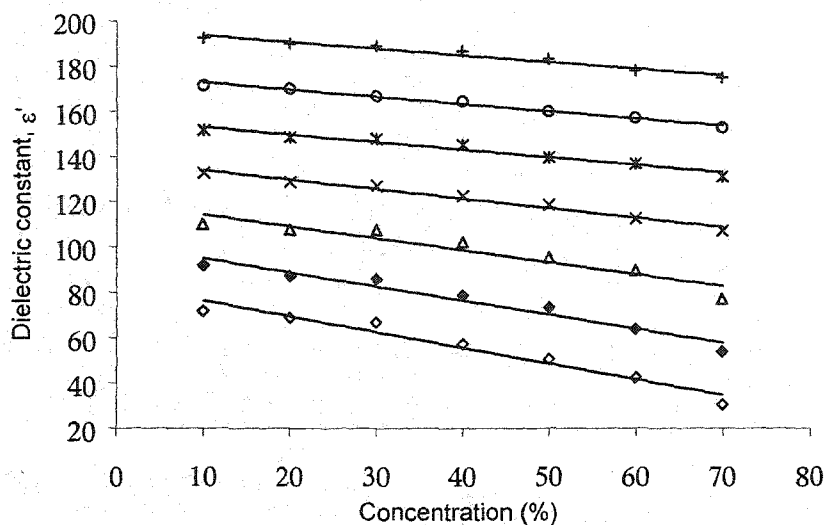


Figure 6.3: Dielectric constant vs concentration of α -D-glucose solutions (+): 85°C, (o): 75°C, (*): 65°C, (x): 55°C, (Δ): 45°C, (\blacklozenge): 35°C, (\diamond): 25°C.

6.4.2 Effect of concentration and temperature on loss factor of α -D-glucose solutions

In contrast to the dielectric constant, the loss factor for 40, 50, and 60% glucose solutions decreased with temperature (Figures 6.4). For other temperature-concentration combinations changes were more complex. For example, at 85°C the loss factor for a 20% or a 30% glucose solution were essentially identical, and similarly for a 10% glucose solution, the loss factor values at 25°C vs. 35°C or 45°C vs. 55°C differed little (Figure 6.4). This may be attributable to mutarotation of the glucose in solution, a complicated process influenced by temperature and concentration. The changes in the structure of the material in solution will result in changes in the loss factor. The variation in ϵ'' with temperature for glucose concentrations of 10, 30 and 50% was found to be linear and highly significant. For the other concentrations studied ϵ'' was found to vary quadratically with temperature. Regression coefficients and coefficients of determination values are presented in Table 6.1. At each temperature the ϵ'' varied exponentially with concentration (Figure 6.5). Regression coefficients and coefficients of determination values are presented in Table 6.2.

Table 6.1: Constants and coefficients of determination of equations relating ϵ' and ϵ'' to temperature (T) at concentrations (Conc.) of 10%-70% α -D-glucose.

Conc. (%)	$\epsilon' = aT + b$			$\epsilon'' = dT^2 + fT + g$			
	<i>a</i>	<i>b</i>	R^2	<i>d</i> ($\times 10^{-3}$)	<i>f</i> ($\times 10^{-1}$)	<i>g</i>	R^2
10	2.0081	21.542	0.9997	0	-0.206	3.685	0.9352
20	2.0361	16.731	0.9997	-0.04	0.393	5.5579	0.9513
30	2.0302	15.634	0.9998	0	-0.435	5.66	0.9511
40	2.1525	4.0916	0.9997	0.2	-0.926	9.2968	0.9942
50	2.1997	-3.636	0.9997	0	-0.758	8.896	0.9930
60	2.2921	-14.41	0.9990	3.9	-6.022	27.966	0.9829
70	2.4440	-30.42	0.9983	-0.4	-0.375	11.577	0.9968

Table 6.2: Constants and coefficients of determination of equations relating ε' and ε'' to α -D-glucose concentration (c) at temperatures (Temp.) of 25-85 °C.

Temp. (°C)	$\varepsilon' = \alpha c + \beta$			$\varepsilon'' = \eta \exp(\gamma c)$		
	α ($\times 10^2$)	β	R^2	γ	η ($\times 10^2$)	R^2
25	-0.5182	77.08	0.9278	2.2235	0.0318	0.9807
35	-0.4569	95.658	0.9282	2.6527	0.0218	0.9671
45	-0.3765	115.04	0.9400	2.3492	0.0199	0.9767
55	-0.3759	136.27	0.9607	2.2135	0.0186	0.9785
65	-0.3397	156.49	0.9582	2.0490	0.0164	0.9683
75	-0.2057	174	0.9698	1.6722	0.0176	0.9544
85	-0.2637	195.31	0.9530	1.3181	0.0146	0.9455

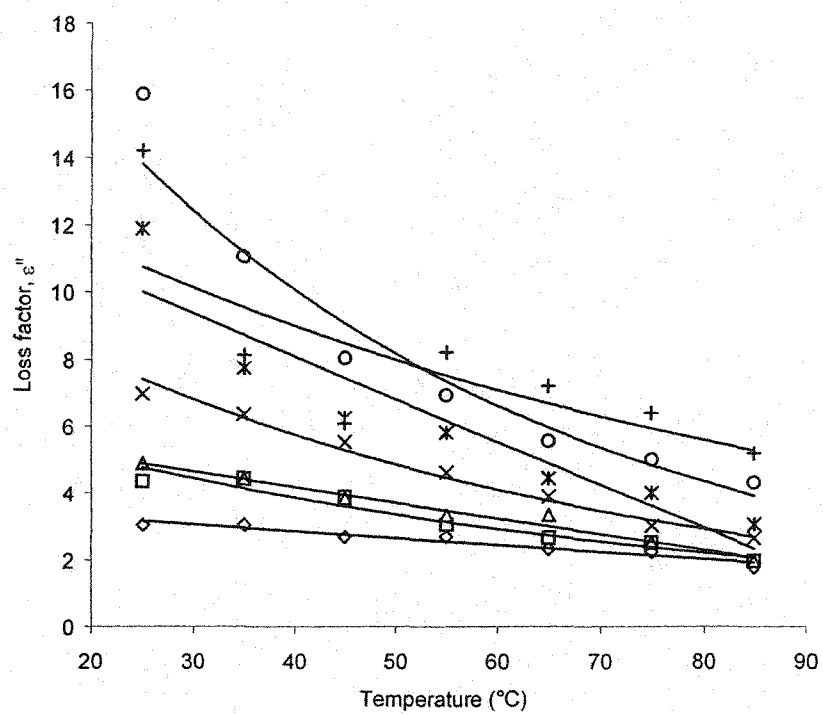


Figure 6.4: Loss factor vs temperature of α -D-glucose solutions (\diamond): 10%; (\square): 20%; (Δ): 30%; (\times): 40%; (*): 50%; (O): 60%; (+): 70%.

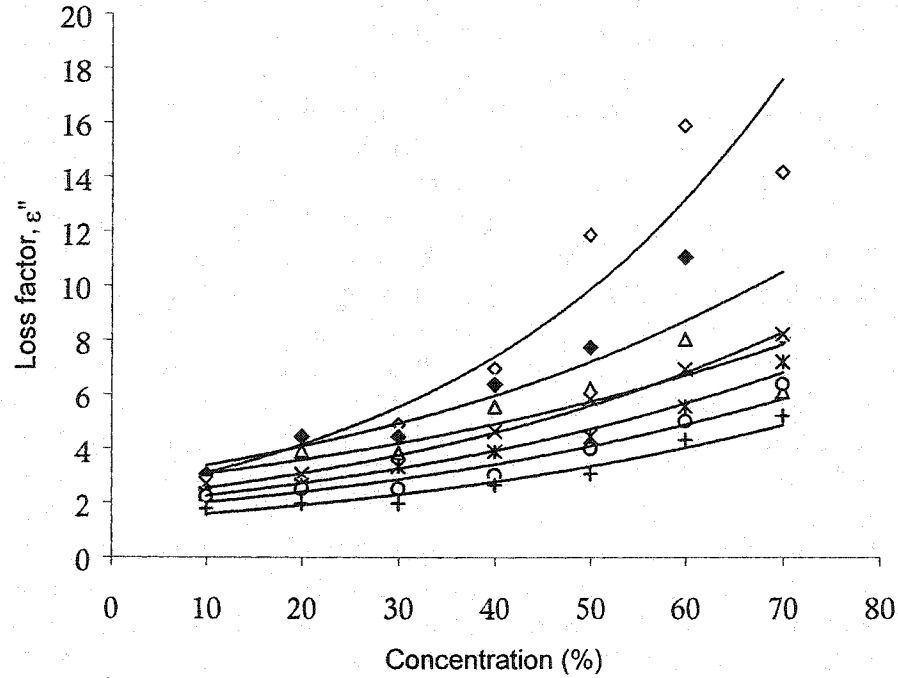


Figure 6.5: Loss factor vs concentration of α -D-glucose solutions (+): 85°C, (o): 75°C, (*): 65°C, (x): 55°C, (Δ): 45°C, (\blacklozenge): 35°C, (\diamond): 25°C.

6.4.3 Predictive models for dielectric properties of α -D-glucose solutions

In order to develop a model to explain ϵ' and ϵ'' as a function of concentration (c) and temperature (T), the data were analyzed using PROC STEPWISE in SAS. The resulting regression models for ϵ' and ϵ'' are given below:

$$\epsilon' = 29 + 1.88T - 43.1c + 0.711Tc - 52.1c^2 \quad (6.1)$$

$$\epsilon'' = -114 + (e^{0.25c} - 1) \times 0.0146T^2 - 0.649Tc + 116e^{0.25c} \quad (6.2)$$

Where, T = temperature, $25 \leq T \leq 85^\circ\text{C}$; c = concentration of glucose solutions, $10\% \leq c \leq 70\%$.

The model for ϵ' and ϵ'' yielded coefficient of determination of 0.9988 and 0.8878 respectively and were both highly significant ($P \leq 0.0001$). Both models could be used to

directly compute the values of dielectric properties of glucose solutions at a given concentration and temperature.

6.5 Conclusions

The dielectric constant and loss factor for α -D-glucose solutions were shown to be dependent on the temperature (25-85°C) and concentration (10-70%). The dielectric constant increased with temperature, but decreased with concentration. At higher temperatures the dielectric constants differed little across glucose concentrations. Loss factor decreased with temperature, but increased with concentration. The variation of the dielectric loss factor was much different from that of dielectric constant. Predictive models were developed to obtain dielectric properties for glucose solutions as functions of both concentration and temperature. These models could be applied to the prediction of microwave heating of chemical reactions involving glucose and water.

Acknowledgments

We are grateful to CIDA (Canadian International Development Agency) and NSERC (National Science Engineering Research Council of Canada) for their financial support.

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CONNECTING TEXT

Results in Chapters IV, V and VI have clearly demonstrated the existence of a good correlation between the dielectric properties of α -D-glucose solutions at both 2450 and 915 MHz and temperature or concentration of the solutions. We have chosen Maillard reaction consisting of glucose, lysine and water as a model system to study at room temperature or under microwave irradiation at 2450 MHz. In order to explain the results obtained by both methods, it is also necessary to know the dielectric data of lysine solution.

The material presented in this chapter will be submitted for publication in a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., Yaylayan, V. A and Wu, G. 2002. Dielectric properties of lysine aqueous solutions at 2450 MHz. *Journal of solution chemistry (to be submitted)*.

The contributions made by different authors are as follows: (i) The first author is the Ph. D student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project, (iii) the fourth author assisted in the experimental work.

VII. DIELECTRIC PROPERTIES OF LYSINE AQUEOUS SOLUTIONS AT 2450 MHz

7.1 Abstract

Dielectric properties of lysine aqueous solutions at 2450 MHz were investigated at concentrations ranging from 9 to 37% (weight percent) at room temperature using a cavity perturbation technique. Dielectric constant decreases with an increase in concentration. Loss factor increases with an increase in concentration at the range of 9 – 31% but decreases at the range of 31-37%. Using PROC GLM in SAS, predictive models are generated to link the dielectric properties to concentrations. The results can be used in estimating the volumetric heating of these solutions by microwave energy, studying the dielectric behavior of the lysine solutions, and optimizing the chemical reactions involving lysine aqueous solutions in a microwave field.

7.2 Introduction

The use of microwave energy in the food industry and in scientific research has opened new vistas due to the fact that it offers numerous advantages in productivity over conventional heating methods such as hot air, steam, etc. These advantages include high speed and efficiency, energy penetration, instantaneous electronic control, selective energy absorption, and clean microwave processing. As we know, according to microwave heating rate equation, the temperature increase depends on the size of the microwave source. In order to maximize this, it would seem desirable to have the electrical field, the frequency and the loss factor of the material as large as possible. In fact, for all practical (commercial) purposes the frequency is limited by the ISM range. Microwave-heating efficiency is directly linked to dielectric properties. Therefore, dielectric properties of material are the key factors to determine the heat behavior of material in the presence of microwave field. Dielectric properties of materials consist of dielectric constant (ϵ') and loss factor (ϵ''). The former, ϵ' , is a measure of the ability of a material to couple with microwave energy and the latter, ϵ'' , is a measure of the ability of

a material to heat by absorbing microwave energy (Mudgett, 1986). Lysine is one of the important amino acids in food chemistry and biological systems. Of all the amino acids, lysine results in the most color in the Maillard reaction, due to its ϵ -amino group and foods containing proteins that are rich in lysine residues are likely to brown readily. Some investigations on the dielectric properties of poly (L-lysine) aqueous solutions exist (Bordi, et al., 1999; 2000a; 2000b). Gusev et al. (1974a; 1974b; 1981) have investigated the dielectric measurement of lysine solutions mainly focusing on dielectric relaxation times. None of them centered on microwave frequency of 2450 MHz for the dielectric properties of lysine aqueous solutions. Furthermore, there are no reports about the relationship between the dielectric properties of lysine aqueous solutions and their concentrations. The dielectric behavior of these specific solutions when exposed to microwaves will not only be useful for microwave-assisted Maillard reaction involving lysine (Liao et al., 2000), but also can help to understand the mechanisms of microwave-enhanced chemical reactions, especially the temperature effect and the changes in dielectric properties before and after reactions.

7.3 Materials & Methods

7.3.1 Materials

DL-Lysine was purchased from SIGMA CHEMICAL CO. (MO, USA) and L-Lysine was obtained from ACROS, New Jersey, USA. Both chemicals were used without further treatment.

7.3.2 Lysine aqueous solutions

The solutions were prepared by adding appropriate amounts of lysine into suitable bottles, which were filled with distilled water to the specific volumes. In order to avoid any effects from disintegration of lysine by microorganisms and precipitation, the measurement was performed immediately.

7.3.3 Dielectric properties measurement

Each sample solution was confined in a 10- μ l sample holder (Borosilicate glass Fisherbrand Micropipets). A cavity perturbation technique at 2450 MHz was used to measure the dielectric properties. The measurement required a dielectric network analyzer (Hewlett Packard), a PC, and measurement cavity. The system software calculated the dielectric parameters from the cavity Q factor, transmission factor (ΔT , the changes in the cavity transmission), and the shift of resonant frequency (ΔF). Details about theoretical measurement background have been reported elsewhere (Meda, 1996; Liao et al., 2001). Before starting measurements, the calibration was verified by taking measurements on a standard liquid (water) with known dielectric properties.

7.3.4 Statistical analysis

Analysis of variance was used to determine differences among the lysine aqueous solutions. Regressions obtained were used to relate dielectric properties and concentrations using PROC GLM in SAS (Version 6.12 for Windows 98).

7.4 Results & Discussion

7.4.1 Dielectric properties of DL and L-Lysine aqueous solutions

The results of the dielectric constant and loss factor of DL and L-Lysine aqueous solutions are shown in Table 7.1.

As shown in Table 7.1, there was no major difference in the dielectric properties for both DL and L-Lysine aqueous solutions at similar concentrations, although the stereochemical compositions of the DL and L-Lysine were different.

Since there were no major differences in the dielectric properties of the DL and L – Lysine aqueous solutions, we focused on the study of dielectric properties of DL-lysine aqueous solutions.

7.4.2 Effect of concentration on dielectric constant of lysine solutions

The effect of concentration on the dielectric constant of lysine solutions is shown in Figure 7.1. Averaged values of six replicates are plotted, as there were no significant

Table 7.1: Dielectric properties of DL and L-Lysine aqueous solutions.

DL-Lysine solutions			L-Lysine solutions		
Con. (%)*	Die. Con.**	Loss Factor	Con. (%)*	Die. Con.**	Loss Factor
28.9	61.0	65.4	29.0	59.4	67.1
21.3	61.1	58.5	21.4	63.3	57.7
14.0	71.2	47.2	14.1	68.1	46.8
10.4	70.3	39.5	10.5	72.1	39.5
9.2	72.9	36.7	9.3	71.6	36.5

*: Concentration of Lysine solution; **: Dielectric constant

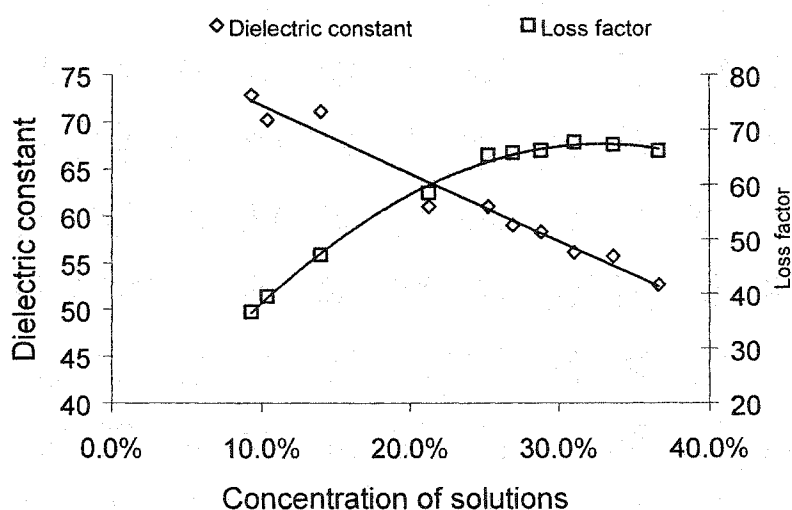


Figure 7.1: Dielectric properties of DL-Lysine aqueous solutions.

differences between the replicates. The dielectric constant decreased with concentration in the concentration range tested (Figure 7.1). The variation in ϵ' with concentration at room temperature was found to be linear and at the 0.0001 significant level with a coefficient of variation (CV) of 5.7%. The constants of the regression line for lysine solutions are shown in Equation 7.1 along with resulting R^2 (coefficient of determination) values as well.

7.4.3 Effect of concentration on loss factor of lysine solutions

The effect of concentration on the loss factor of lysine solutions is also shown in Figure 7.1. Contrary to the dielectric constant, the loss factor increased with an increase in concentration at the range of 9-31% but decreased at the range of 31-37% (Figure 7.1). The reason for this may result from the number of the free molecules in the solutions and the interaction of water and lysine. The variation in ϵ'' with concentration at room temperature was found to be quadratic and significant at 0.0001 level with a coefficient of variation (CV) of 2.3%. The constants of the regression curve for lysine solutions are presented in Equation 7.2 along with the resulting R^2 (coefficient of determination) values.

In this type of solutions, we found that the loss tangent is less than 1 in lower concentration (<21%), while it is higher than 1 in the higher concentration (>21%). It differs to the previous results for alcohols and glucose solutions studied in this project. For the loss tangents of alcohols and glucose, they are less than 1 in all experiments. This unexpected result will have some profound effects on heat distribution and temperature profile of the lysine solution under microwave irradiation.

7.4.4 Predictive models for dielectric properties of lysine solutions

In order to develop a model to explain ϵ' and ϵ'' as function of concentration (c), the data were analyzed using PROC GLM in SAS. The resulting regression models for ϵ' and ϵ'' are given below:

$$\begin{aligned}\epsilon' &= -70.08c + 78.44 \\ (R^2 &= 0.7253)\end{aligned}\tag{7.1}$$

$$\begin{aligned}\epsilon'' &= -581.52c^2 + 376.76c + 6.43 \\ (R^2 &= 0.9737)\end{aligned}\tag{7.2}$$

Where, c = concentration of glucose solutions, $9\% \leq c \leq 37\%$.

Both models could be directly used to compute the values of dielectric properties of lysine solutions at varying concentrations.

7.5 Conclusions

Dielectric constant and loss factor for lysine aqueous solutions were shown to be dependent on the concentration. The dielectric constant decreased with an increase in concentration. Loss factor increased with concentration at the concentration range of 9-31%. There were some differences in loss tangent of lysine solutions compared to those solutions studied in this project. This information can be efficiently utilized in the microwave heating to get the different temperature profile.

Acknowledgments

We are grateful to CIDA (Canadian International Development Agency) and NSERC (National Science Engineering Research Council of Canada) for their financial support.

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CONNECTING TEXT

In Chapters III–VII, we concluded that there was excellent relationship between dielectric properties of chemicals and their concentration or temperature. Due to the existence of the relationships between dielectric properties of solutions and their concentrations (or constitutions) and the changes in the concentrations of the reactants and products, the direct application of dielectric properties to chemical reactions will be presented in the next two chapters. It includes the use of dielectric properties to determine the yield of the esterification (theoretical model in Chapter VIII) and the kinetic study of the Maillard reaction from the point of view of dielectric properties in Chapter IX.

The material presented in this chapter is being evaluated by a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2002. Application of dielectric properties in esterification. *Angewandte Chemie International Edition*.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

VIII. APPLICATION OF DIELECTRIC PROPERTIES IN ESTERIFICATION

8.1 Abstract

The dielectric properties of the esterification model system were investigated. The relationship between dielectric properties and the theoretical reaction yield is presented. Theoretically, with the use of this relationship one can monitor the reaction yield during the reaction process; hence it is useful in the design consideration for the product development.

8.2 Introduction

The yield of the chemical reaction is one of the most important factors for determining the applicability in industry. Many methods have been developed to detect the yield or monitor the process during the chemical reaction, such as UV/VIS (ultra-violet/visible) spectrophotometer, HPLC (high performance liquid chromatograph), NMR (nuclear magnetic resonance), LC (liquid chromatograph), and GC-MS (gas chromatograph-mass). In addition, dielectric property measurement of materials is also an important area of development in academic, governmental, company, and industrial laboratories today. Dielectric properties are intrinsic characteristics of the materials explaining the behavior and degree of the wave-material interaction when exposed to microwave field. They are very important in microwave heating, microwave sensing, processing design and application. There are many researchers who have used dielectric properties to measure the moisture content of agri-food. Meda et al. (1998) have studied the dielectric properties of grain. Kraszewski et al. (1989) have used microwave data to measure the moisture content of soybean seeds. Kraszewski and Nelson (1993; 1994) employed the same technology to determine the moisture content and mass of peanut and wheat kernels. Okamura and Zhang (2000) developed a new method to measure the moisture content of the material by using phase shift at two microwave frequencies. Bernou et al. (2000) developed microwave sensor for humidity detection using the electromagnetic property variation of some sensitive materials in the presence of gas at

microwave frequency (ca. 1 GHz). Nelson et al. (1995) showed the existence of some relationship between the dielectric properties and maturity of some fruits. Buchner and Barthel (1995) studied the kinetic process in the liquid phase by making use of the dielectric properties of the materials. Rudakov (1997; 1998) used dielectric properties of the solvents to optimize the mobile phase in the high-performance liquid chromatography. Martens et al. (1993) proposed that the use of a microwave (20-100 GHz) confocal resonator to accomplish the detection of the electromagnetic and chemical properties of material. In addition, at the fundamental level, the dielectric behavior of the material can provide the information about molecular interactions and mechanism of molecular processes (Firman et al., 1991; Lunkenheimer and Loidl, 1996; Matsuoka et al., 1997). Suzuki et al. (1996; 1997) used dielectric analysis to study the hydration of protein in solution and hydrophobic hydration of amino acid solutions. Shinyashiki et al. (1998) investigated the dynamic of water in a polymer matrix studied by making use of microwave dielectric analysis. Recently, it has been used as the chemical sensor to measure the solution concentration (McKee and Johnson, 2000).

In this paper, a new method to determine the yield of the chemical reaction is proposed. The method presented is based on the dielectric properties (dielectric constant and loss factor) of the materials at microwave frequencies of 2450 and 915 MHz. It has two characteristics. One is the shift in the resonant frequency. The other is the shift in Q factor of the cavity when the object is inserted into the cavity (Donoven et al., 1993; Klein et al., 1993; Dressel et al., 1993). Dielectric properties (dielectric constant and loss factor) are key parameters of materials. They are dependent on the composition of material. In this research, a cavity perturbation technology to measure the dielectric properties was employed due to its simplicity of the measurement set-up, high sensitivity, automated experimental facility, direct evaluation and higher accuracy. It does not require complicated calibration since a network analyzer can accomplish most of the sensing functions (Chen et al., 1999). A simple cavity can be created with a hollow rectangular or circular wave-guide. The dielectric properties of material are determined by measuring the shift in the resonant frequency and the change in the Q factor of the cavity when a sample is introduced into the cavity. The dielectric properties (dielectric constant and loss factor) are given by:

$$\varepsilon' = 1 + \frac{(f_o - f_s)V_o}{2kf_oV_s} \quad (8.1)$$

$$\varepsilon'' = \frac{V_o}{4k^2V_s} \times \left(\frac{1}{Q_s} - \frac{1}{Q_o} \right) \quad (8.2)$$

Where, subscripts o and s refer to the empty cavity and the cavity loaded with an object at the centre of the cavity, V= volume, f = resonant frequency, Q=Q factor, k= factor dependent upon object shape, orientation and permittivity.

The dielectric properties of materials measured depend on the volume, geometry, dimension, location, its composition and mode of operation of the cavity. For a circular cavity, the dielectric properties of solutions relate to the composition of the material.

8.3 Materials & Method

8.3.1 Reagents

p-Toluenesulfonic acid, *p*-hydroxybenzoic acid, methylparaben, *n*-propylparaben, *n*-butylparaben, 1-butanol, methanol were purchased from Sigma Chemical Co. (St. Louis, MO, USA). 1-propanol was obtained from Aldrich chemical Co. Inc (Milwaukee, WI, USA). All chemicals were of analytical grade reagents.

8.3.2 The yield definition

The yield of this specific reaction (Esterification of parahydroxybenzoic acid with methanol, 1-propanol, and 1-butanol, respectively) is defined as:

$$\eta = \frac{n_1}{n_2} \times 100\% \quad (8.3)$$

Where n_1 and n_2 are the mole number of the product (paraben) and original reactant (parahydroxybenzoic acid), respectively.

8.3.3 Sample preparation and dielectric property measurement

Model solutions representing different percentage yields of esters (0, 30, 50, 70 and 90% yields) were prepared by mixing *p*-hydroxybenzoic acid with alcohols and their corresponding esters and water in amounts calculated based on the above mentioned theoretical yields. The above solutions were immediately analyzed for the dielectric properties by cavity perturbation technique (Liao et al., 2001). Due to the limited solubility, it was impossible to prepare solutions with the ratio less than 5. The ratio refers to the mole number of alcohol to the mole number of *p*-hydroxybenzoic acid. 10% of the PTSA, a catalyst, was added to the mimicked system.

8.3.4 Statistical analysis

Three samples were used for each reaction. Regressions relating the yield and dielectric properties (dielectric constant and loss factor) of the chemical reaction were obtained using PROC STEPWISE in SAS (Version 6.12 for Windows 98).

8.4 Results & Discussion

8.4.1 Dielectric constant as a function of yield at both 2450 and 915 MHz

The data indicate the absence of a relationship such as linear or quadratic between resonant frequency and the corresponding yields. Therefore, it is not possible to correlate the dielectric constant with the yield of the reaction due to the fact that the dielectric constant is mainly dependent on the amount of frequency shift (Equation 8.1). Further, the dielectric constant of the model system irregularly changed with the yield. A representative relation is shown in Figures 8.1 and 8.2, respectively.

8.4.2 Loss factor as a function of yield at both 2450 and 915 MHz

Contrary to the relation seen for dielectric constant, there could be regular trends such as quadratic linking quality factor to the corresponding yields. Therefore, attempt is made to correlate the loss factor with the yield of the reaction. The loss factor is mainly dependent on the amount of the shift in *Q* factor (Equation 8.2). The relations are shown for the *Q_s* factor vs yield and loss factor vs yield in Figures 8.3 and 8.4, respectively. The

Q_s increases with the yield in a smooth way, while the corresponding loss factor does inverse.

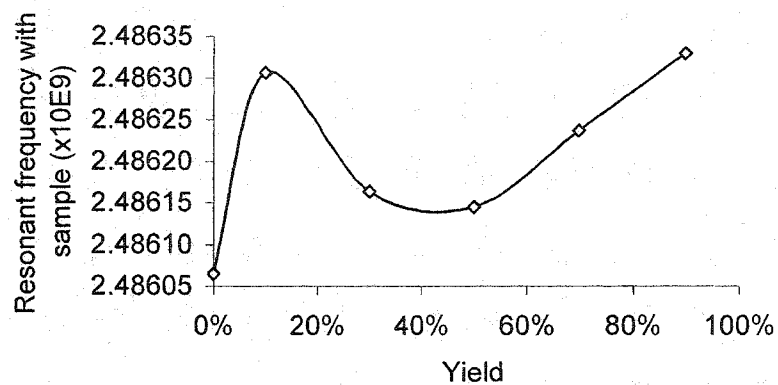


Figure 8.1: Variation of resonant frequency of loaded sample at 2450 MHz as a function of yield when alcohol is methanol.

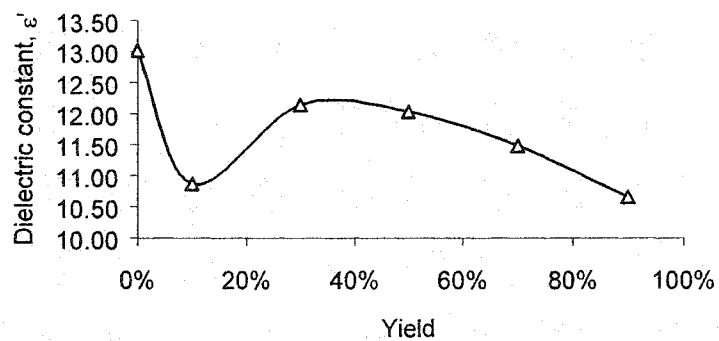


Figure 8.2: Variation of dielectric constant of loaded sample at 2450 MHz as a function of yield when alcohol is methanol.

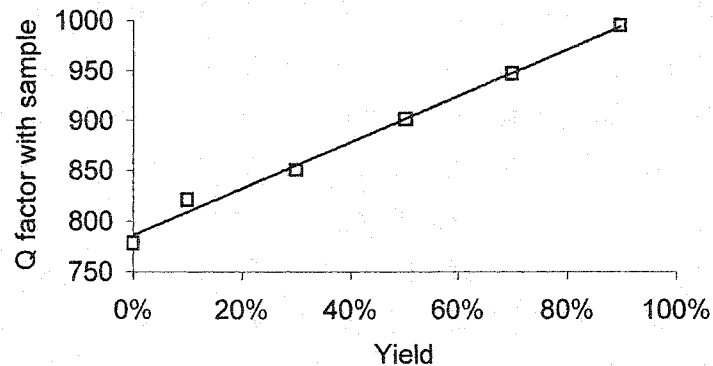


Figure 8.3: Variation of Q factor of loaded sample at 2450 MHz as a function of yield when alcohol is methanol.

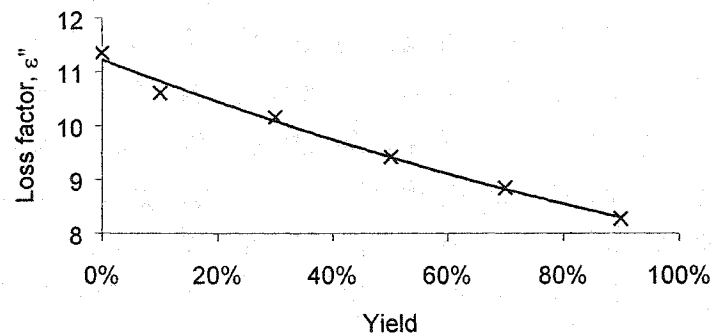


Figure 8.4: Variation of loss factor of loaded sample at 2450 MHz as a function of yield when alcohol is methanol.

8.4.3 The predictive models for the Q_s factor, dielectric loss factor and the theoretical yields

To obtain relations of Q_s factor and dielectric loss factor with the theoretical yields of the different types of esterification, SAS was used. The results are presented in Tables 8.1, 8.2, and 8.3. All esterification model systems can be described by the quadratic equations. The models could be used to determine the yield of esterification after

measuring the loss factor or to estimate the dielectric loss factor after measuring the yield of the reaction.

**Table 8.1: Predictive equations for the esterification model systems
when alcohol is methanol**

Ratio	2450 MHz		915 MHz	
	Equations	R ²	Equations	R ²
7:1	$Q_s = 785.99 + 231.38\eta$	0.9910	$Q_s = 2026.04 + 356.24\eta - 138.29\eta^2$	0.9942
	$\epsilon'' = 11.23 - 4.06\eta + 0.89\eta^2$	0.9877	$\epsilon'' = 14.76 - 6.67\eta + 2.87\eta^2$	0.9597

**Table 8.2: Predictive equations for the esterification model systems
when alcohol is 1-propanol**

Ratio	2450 MHz		915 MHz	
	Equations	R ²	Equations	R ²
5:1	$Q_s = 1896.43 - 195.92\eta^2$	0.9366	$Q_s = 2654.74 - 75.65\eta^2$	0.9450
	$\epsilon'' = 2.97 + 0.6755\eta^2$	0.9456	$\epsilon'' = 5.13 + 0.8897\eta^2$	0.9446
7:1	$Q_s = 1882.65 - 195.92\eta$	0.9904	$Q_s = 2620.71 - 56.59\eta^2$	0.9589
	$\epsilon'' = 2.99 + 0.6987\eta$	0.9819	$\epsilon'' = 5.53 + 0.6775\eta^2$	0.9597

**Table 8.3: Predictive equations for the esterification model systems
when alcohol is 1-butanol**

Ratio	2450 MHz		915 MHz	
	Equations	R ²	Equations	R ²
5:1	$Q_s = 2491 - 835.68\eta + 453.75\eta^2$	0.9219	$Q_s = 2866 - 152.27\eta + 38.09\eta^2$	0.9909
	$\epsilon'' = 1.66 + 1.67\eta - 0.8478\eta^2$	0.9252	$\epsilon'' = 3.0435 + 2.136\eta - 0.9973\eta^2$	0.9446
7:1	$Q_s = 2447 - 737.92\eta + 394.63\eta^2$	0.9495	$Q_s = 2846 - 188.34\eta + 82.78\eta^2$	0.9537
	$\epsilon'' = 1.735 + 1.529\eta - 0.774\eta^2$	0.9519	$\epsilon'' = 3.22 + 1.90\eta - 0.81\eta^2$	0.9538

Where, ratio refers to the mole number of alcohol to the mole number of para-hydroxybenzoic acid; Q_s is the resonant frequency with sample; ϵ'' is the loss factor; η is the theoretical reaction yield (%); all regression models are significant at 0.0001 level.

8.5 Conclusions

The dielectric properties of esterification model systems were investigated with respect to the theoretical yields. It is possible to correlate the Q_s factor or loss factor with the yield of the reaction. The results have shown additional use of the application of loss factor in the chemical reaction and microwave assisted chemical engineering.

Acknowledgment

We thank the financial support from CIDA (Canadian International Development Agency) and NSERC (National Science and Engineering Research Council of Canada).

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CONNECTING TEXT

In Chapter VIII, we found good relationships between the dielectric loss factor and the theoretical yield of the reaction. The next step is to explore the Maillard reaction model system.

In this chapter we will demonstrate that it is also possible to use dielectric loss factor and loss tangent to study Maillard reaction model system if the appropriate system is chosen.

The material presented in this chapter will be submitted for publication in a peer-reviewed journal (see details of publication below)

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2002. Use of dielectric properties to study the Maillard reaction model system. *Journal of food Science (to be submitted)*.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

IX. USE OF DIELECTRIC PROPERTIES TO STUDY THE MAILLARD REACTION MODEL SYSTEM

9.1 Abstract

The Maillard reaction model system consisting of glucose and lysine in water was investigated at room temperature. The relationships of the dielectric properties (dielectric constant, loss factor), and loss tangent with reaction time and ratio of the reactants will be established. Quality aspects like absorbance and color development will be studied as well. All these will assist in establishing relevance of using loss factor and loss tangent in kinetics of reactions.

9.2 Introduction

Maillard reaction, which was named after its inventor, Lois-Camille Maillard, is one of the major reactions related to the formation of food flavors and colors during the thermal processing. It involves the reaction of amines with carbonyl compounds, especially reducing sugars. It is necessary to monitor or trail the kinetic behavior of Maillard reactions in food and pharmaceutical industries using simple and rapid methods. Much effort has been made to study this type of chemical reactions (Van Boekel, 2001). Because the Maillard reaction can result in some distinctive compounds, which can produce colors in solvents, the use of spectrophotometry and colorimetry has been studied. In Hutchings' review (1994), he reported that most researchers used only selected wavelengths (420-460 nm) to study this reaction. Maillard model systems containing lysine and sugars in solution can be monitored by lysine oxidase electrodes (Assoumani et al., 1990) or by spectrophotometric techniques (Westphal et al., 1988). Ge and Lee (1996) developed a method to determine Amadori compounds of phenylalanine, tryptophan, and tyrosine and their parent compounds simultaneously in the Maillard reaction mixture by using HPLC with an UV detector and a pulsed amperometric detector. MacDougall and Granov (1998) reported that using a Hunter Colorquest Dio-Array Spectrophotometer to measure the color development in CIELAB (Commission

Internationale d'Eclairage LAB) space. Twenty colored fractions were revealed by Hofmann (1998) using color dilution analysis methods (CDA). However, we have found that microwave resonant cavity measurements provide an interesting alternative, because they are fast, accurate and do not require further treatment after reaction. This emerging technique, which is currently a combinatory application of physics and chemistry, is based on measurement of the resonant frequency and Q factor shift.

A product responding to microwaves depends on its dielectric properties, which are associated with temperature, water activity and polarity (Decareau, 1985; Mudget, 1986). The lower the molecular weight of a compound is, the greater will the behavior of its interaction with microwaves. Although Assoumani et al. (1994) first developed a real-time non-destructive microwave spectral analysis method (2400 MHz-2450 MHz) to study a Maillard model system at various lysine-glucose ratios; they did not use this method for the kinetic studies of this Maillard model system. In addition, the correlated relationship between the ratio and another microwave frequency such as 915 MHz is not studied at all. Therefore, the objective of the present work is to develop an analysis method to study the kinetic behavior of a Maillard model system at various lysine/glucose ratios at both 915 and 2450 MHz from the point of view of dielectric properties. The decision for the better factors (dielectric constant, dielectric loss factor, loss tangent, Quality factor, and resonant frequency) to use for these kinetic studies will be discussed. The kinetic model involving the loss factor, the ratio of the reactants and the reaction time will be established.

9.3 Materials and Methods

9.3.1 Reagents

L-lysine HCl was purchased from ACROS ORGANICS (New Jersey, USA). α -D-glucose was obtained from Sigma Chemicals Company (St Louis, MO).

9.3.2 Reaction mixture

The mixtures were prepared by dissolving 2.5-2.6 g of glucose and varying level of lysine in 2-ml water. The ratio of the reactants [(lysine (g)/glucose (g))] was 0.71, 0.54, 0.42, 0.37 and 0.23. Because 2.5-2.6 g of glucose could not be completely dissolved in 2

g of water at room temperature, microwave heating was used to aid the dissolution of glucose in water. After microwave heating, the sample was kept at room temperature for four hours and was found that there was no precipitation in the solution. After that, different amounts of lysine were added to reach the desired ratio of the reactants.

All mixtures were placed in 4-ml vials closed with a rubber stopper and kept at room temperature up to 107 hours. Samples (0.4-ml) were taken at specific time intervals, and diluted by the addition of 2-ml water. Samples for dielectric property measurement were used without dilution. In order to avoid further reaction, the diluted samples and those sample holders loaded with sample were stored at 4 °C before measuring dielectric properties, color, absorbance at 420 and 287 nm at room temperature.

9.3.3 Absorbance measurement

The color intensity of the samples was measured at 287 nm using a Beckman DU-64 Spectrophotometer. The optical density (OD) was also measured at 420 nm.

9.3.4 Colour measurement

Colour was measured in CIELAB space by using a Chroma Meter (Minolta Chroma Meter, CR-200b, Minolta Camera Co. Ltd., Azuchi-Machi, Chuo-Ku, Osaka 541, Japan). The diluted samples were placed inside a vial for colorimetric assessment of the reaction mixture. The Chroma Meter was calibrated against a standard calibration plate of a white surface with L*, a* and b* value according to manufacture's recommendations. The measurements were repeated six times for each sample. Data are reported as L*, uniform lightness and the chromaticness coordinates a* (+ red to - green) and b* (+ yellow to - blue).

9.3.5 Dielectric properties measurement

A Hewlett Packard 8753D dielectric network analyzer having a frequency range of 30 kHz to 6 GHz was used. The resolution is 1 Hz. The resonator cavities were made of copper with volume of 264749 mm³ for 2450 MHz and 1922876 mm³ for 915 MHz. The cavity is attached to the network analyzer with co-axial cables, which emitted the microwave power and frequency to the sample. The system was calibrated with distilled

water, a liquid of known dielectric properties. The sample was confined in a 10 μ l borosilicate glass sample holder (Fisherbrand Micropipet). Three consecutive measurements were performed at ambient temperature to obtain the resonant frequency (f), Q factor, dielectric constant, and loss factor. Details about measurement, theoretical background and methodology have been reported elsewhere (Kraszewski and Nelson, 1993, 1994; Liao et al., 2001).

9.4 Results & Discussion

9.4.1 Colour development

CIELAB lightness (L^*) and Chroms (a^* , b^*) of the color development for the reaction mixture are shown in Tables 9.1-9.5. The progress of the lightness (L^*) is also given in Figure 9.1. The effect of the ratio of the reactants and the reaction time are clearly illustrated. Although there is no behavior with the reaction time that can be predicted from the ratio tested, the lightness of all the samples tested were, in some sense, lost after 107 hours at room temperature.

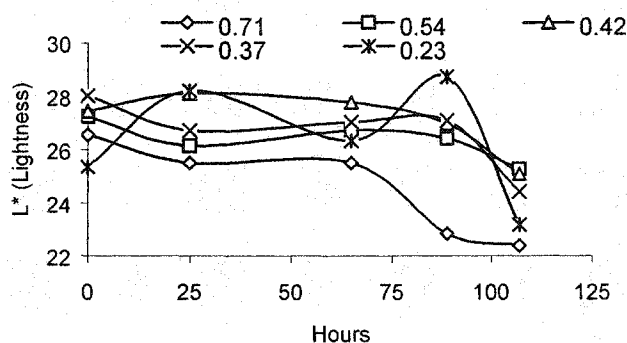


Figure 9.1: CIELAB Lightness (L^*) plots of color development of glucose and lysine mixture in water at room temperature.

The development of the chroma of the colors is shown in the a^* , b^* diagrams (Figure 9.2). Most variations in a^* first move towards greenness, along the a^* negative axis and then it moves towards redness, along the a^* positive axis. Contrary to variation in a^* , most variations in b^* , first moves towards yellowness, along the b^* positive axis and then generally decreases in b^* positive axis. (Also see the value in Tables 9.1–9.5). The location of the individual colors in Figure 9.2 is linked to the lysine and glucose concentration. The chroma diagrams for the different ratio of the reactants were not identical, indicating that the

sequence of the Maillard pigments formed during their respective reaction were not the same. This observation is in agreement with the previous report by MacDougall and Granov (1998).

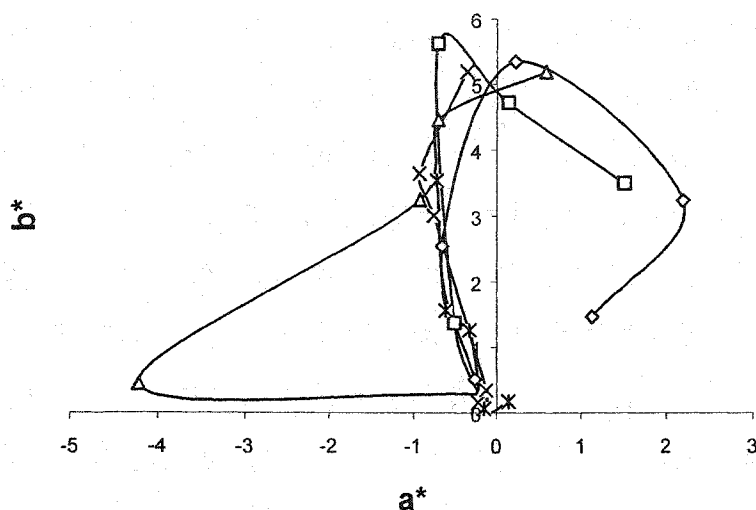


Figure 9.2: CIELAB chroma (a^* , b^*) plots of color development of glucose and lysine mixture in water at room temperature (\diamond): 0.71; (\square): 0.54; (Δ): 0.42; (\times): 0.37; ($*$): 0.23.

9.4.2 Absorbance at 287 nm (A_{287}) and 420 nm (A_{420})

The visual browning of the model system depends on both the ratio of the reactants and the reaction time at room temperature. A_{287} and A_{420} are shown in Tables 9.1-9.5. The absorbance at both wavelengths increased with time. However, the increment for A_{287} became very small after 65 hours except when the ratio was 0.23.

Table 9.1: Color development and absorbance with time when the reactant ratio is 0.71.

Time(h)	L^*	a^*	b^*	A_{420}	A_{287}
0	26.55	-0.26	0.51	0.08	1.47
25	25.51	-0.65	2.54	0.28	2.87
65	25.51	0.23	5.34	2.53	2.92
89	22.84	2.20	3.24	3.42	2.93
107	22.39	1.13	1.47	3.70	2.95

Table 9.2: Color development and absorbance with time when the reactant ratio is 0.54.

Time(h)	L*	a*	b*	A ₄₂₀	A ₂₈₇
0	27.23	-0.18	0.18	0.04	0.75
25	26.14	-0.50	1.37	0.13	1.61
65	26.72	-0.70	5.62	1.20	2.91
89	26.42	0.14	4.71	1.95	2.95
107	25.27	1.51	3.50	3.32	3.00

Table 9.3: Color development and absorbance with time when the reactant ratio is 0.42.

Time(h)	L*	a*	b*	A ₄₂₀	A ₂₈₇
0	27.44	-0.20	0.29	0.03	0.55
25	28.11	-4.22	0.43	0.07	1.07
65	27.78	-0.92	3.25	0.46	2.93
89	26.96	-0.70	4.46	0.85	2.96
107	25.09	0.59	5.19	1.97	3.01

Table 9.4: Color development and absorbance with time when the reactant ratio is 0.37.

Time(h)	L*	a*	b*	A ₄₂₀	A ₂₈₇
0	28.02	-0.21	0.16	0.03	0.60
25	26.72	-0.12	0.34	0.05	0.85
65	27.03	-0.76	3.01	0.36	2.85
89	27.09	-0.92	3.65	0.68	2.99
107	24.43	-0.35	5.19	1.01	2.97

Table 9.5: Color development and absorbance with time when the reactant ratio is 0.23.

Time(h)	L*	a*	b*	A ₄₂₀	A ₂₈₇
0	25.35	0.14	0.17	0.02	0.36
25	28.20	-0.14	0.06	0.03	0.56
65	26.34	-0.32	1.26	0.13	1.79
89	28.74	-0.61	1.56	0.20	2.31
107	23.17	-0.72	3.54	0.44	2.96

9.4.3 The dielectric constant, loss factor and loss tangent

9.4.3.1 At 2450 MHz

The average values for the resonant frequency (f_s), Q factor (Q_s), dielectric constant (ϵ'), loss factor (ϵ'') and loss tangent ($\tan\delta$) for the reaction systems with the different reactant ratios at room temperature with time are shown in Tables 9.6-9.10, respectively.

Table 9.6: Microwave data for 0.71 ratio of the reaction system at 2450 MHz.

Hours	$f_s (\times 10^9)$	Q_s	ϵ'	ϵ''	$\tan\delta$
0	2.479739	571.89	67.61	16.54	0.2446
25	2.479743	599.51	67.57	15.65	0.2316
65	2.479799	596.83	67.07	15.73	0.2345
89	2.479850	596.26	66.62	15.75	0.2364
107	2.479897	549.54	66.20	17.32	0.2616

Table 9.7: Microwave data for 0.54 ratio of the reaction system at 2450 MHz.

Hours	f_s ($\times 10^9$)	Q_s	ϵ'	ϵ''	$\tan\delta$
0	2.479696	603.03	67.99	15.54	0.2286
25	2.479617	635.59	68.71	14.60	0.2125
65	2.479798	628.87	67.08	14.79	0.2205
89	2.479657	646.44	68.26	14.31	0.2096
107	2.479741	597.15	67.59	15.22	0.2252

Table 9.8: Microwave data for 0.42 ratio of the reaction system at 2450 MHz.

Hours	f_s ($\times 10^9$)	Q_s	ϵ'	ϵ''	$\tan\delta$
0	2.479694	677.25	68.02	13.50	0.1985
25	2.479636	673.46	68.70	13.66	0.1988
65	2.479600	679.79	68.86	13.47	0.1956
89	2.479686	687.15	68.09	13.30	0.1953
107	2.479820	660.99	66.89	13.93	0.2083

Table 9.9: Microwave data for 0.37 ratio of the reaction system at 2450 MHz.

Hours	f_s ($\times 10^9$)	Q_s	ϵ'	ϵ''	$\tan\delta$
0	2.479890	651.48	66.26	14.18	0.214005
25	2.479603	688.56	68.81	13.26	0.192705
65	2.479631	689.62	68.58	13.24	0.193059
89	2.479777	686.62	67.27	13.34	0.198305
107	2.479630	714.55	68.58	12.68	0.184894

Table 9.10: Microwave data for 0.23 ratio of the reaction system at 2450 MHz.

Hours	$f_s (\times 10^9)$	Q_s	ϵ'	ϵ''	$\tan\delta$
0	2.479660	730.66	68.32	12.34	0.1806
25	2.479613	728.42	68.74	12.39	0.1802
65	2.479652	732.79	68.41	12.30	0.1798
89	2.479758	754.84	67.44	11.85	0.1757
107	2.479708	724.63	67.89	12.46	0.1835

As observed from the data in the tables 9.6-9.10, the variation in microwave data is dependent on the reaction time and ratio of the reactants. However, there were no major changes with the reaction time in resonant frequency, dielectric constant, Q_s factor and loss factor for all the reaction mixtures tested except when the reactant ratio is 0.71. There is no relationship between the microwave data with time at the specific ratio except when the reactant ratio is 0.71 (or higher concentration of reactants in this case). The reason for this observation may be due to the presence of excess water in the system. Pure water has higher dielectric constant (~ 80) and loss factor (~ 10) at 2450 MHz. This means that even if some chemical reactions are occurring in the lower reactant ratio (or in lower concentration of reactants in this case); it is still difficult to detect the changes in dielectric properties with reaction time. The results obtained from the SAS analysis for loss factor and loss tangent are shown in Table 9.11.

Further, relationships between loss factor (ϵ'') versus ratio (c) and loss tangent ($\tan\delta$) versus ratio (c) were established. The results obtained from the SAS analysis are presented in Table 9.12. All relationships are good. However, the relationship obtained from the experimental data could be used to study the kinetics of this reaction only when the reactant ratio or the concentration of the reactants is high enough as the dielectric properties of this system are mainly dependent on the concentration of water.

Table 9.11: Regression Equation constants and coefficients of determination (R^2) of the equations for the Maillard reaction model system consisting of glucose and lysine in water with time (hours) at different ratios at 2450 MHz.

Ratio	Dielectric loss factor			R ²	Loss tangent			R ²
	A ₁ × t ² + b ₁ × t + c ₁				a ₂ × t ² + b ₂ × t + c ₂			
	a ₁	b ₁	c ₁		A ₂	b ₂	C ₂	
0.71	0.0005	-0.0506	16.5759	0.8327	0.000008	-0.000757	0.24523	0.8132
0.54	0.0003	-0.0352	15.4798	0.6488	0.000004	-0.000491	0.22684	0.4430
0.42	0.0001	-0.0082	13.6102	0.1977	0.000003	-0.000264	0.20031	0.5045
0.37	0.0001	-0.0165	13.9915	0.6942	0.000002	-0.000421	0.20980	0.5859
0.23	0.0001	-0.0073	12.4160	0.1330	0.000001	-0.000122	0.18144	0.1785

Table 9.12: Regression equation constants and coefficients of determination (R^2) of the equations for the Maillard reaction model system consisting of glucose and lysine in water with ratio at the tested time at 2450 MHz.

Time	Dielectric loss factor			R ²	Loss tangent			R ²
	A ₃ × c ² + b ₃ × c + c ₃				a ₄ × c ² + b ₄ × c + c ₄			
	a ₃	b ₃	c ₃		A ₄	b ₄	c ₄	
0	-2.6746	11.3570	9.8853	0.9231	-0.0615	0.18883	0.14185	0.8832
25	-0.2811	7.1912	10.7132	0.9934	0.0299	0.08018	0.15986	0.9860
65	-0.2724	7.6866	10.4794	0.9798	0.0185	0.10332	0.15349	0.9645
89	-0.5363	8.3937	10.0247	0.9804	0.0466	0.07682	0.15741	0.9530
107	11.8300	-0.4752	11.7921	0.9693	0.2116	-0.0287	0.17663	0.9567

In order to better describe the variation in dielectric loss factor and loss tangent for those reaction mixtures tested, we analyzed the data obtained by using PROC STEPWISE in SAS. We found a good relationship amongst dielectric loss factor, loss tangent, ratio of the reactants and reaction time at room temperature. The regression models can be expressed by:

$$\varepsilon'' = 2.04 \times 10^{-4} t^2 + 1.49 \times 10^{-2} tc - 3.03 \times 10^{-2} t + 7.50c + 11.00 \quad (9.1)$$

($R^2=0.9299$)

$$\tan \delta = 3.76 \times 10^{-6} t^2 + 3.08 \times 10^{-4} tc + 4.90 \times 10^{-2} c^2 - 5.51 \times 10^{-4} t + 6.64 \times 10^{-2} c + 0.17$$

$$(R^2=0.9137) \quad (9.2)$$

Where, t is reaction time (0-107 hours); c is the ratio of the reactants (0.23-0.71).

Both equations obtained were found to be very significant at 0.0001 level. Therefore, it is possible to use both models to study the kinetics of this type of chemical reaction when the reaction mixture is concentrated.

9.4.3.2 At 915 MHz:

The average value of the resonant frequency (f_s), Q factor (Q_s), dielectric constant (ϵ'), loss factor (ϵ'') and loss tangent ($\tan \delta$) for the reaction systems with the different reactant ratios at room temperature with time is presented in Tables 9.13-17, respectively.

Table 9.13: Microwave data for 0.71 ratio of the reaction system at 915 MHz.

Hours	f_s	Q_s	ϵ'	ϵ''	$\tan \delta$
0	9.279000	1779.47	81.15	17.98	0.2215
25	9.278980	1830.21	81.57	16.72	0.2050
65	9.279030	1810.31	80.72	17.21	0.2132
89	9.279040	1807.34	80.43	17.28	0.2149
107	9.279080	1712.67	79.72	19.74	0.2476

Table 9.14: Microwave data for 0.54 ratio of the reaction system at 915 MHz.

Hours	f_s	Q_s	ϵ'	ϵ''	$\tan \delta$
0	9.278964	1842.43	81.82	16.43	0.2008
25	9.278973	1921.30	81.66	14.64	0.1793
65	9.279072	1895.00	79.94	15.22	0.1904
89	9.279036	1931.02	80.56	14.43	0.1792
107	9.279024	1863.20	80.77	15.95	0.1975

Table 9.15: Microwave data for 0.42 ratio of the reaction system at 915 MHz.

Hours	f_s	Q_s	ϵ'	ϵ''	$\tan\delta$
0	9.279032	2020.69	80.61	12.59	0.1562
25	9.279017	2009.06	80.89	12.82	0.1585
65	9.278993	2003.63	81.29	12.92	0.1590
89	9.279033	2004.77	80.60	12.90	0.1601
107	9.279036	1957.20	80.55	13.88	0.1723

Table 9.16: Microwave data for 0.37 ratio of the reaction system at 915 MHz.

Hours	f_s	Q_s	ϵ'	ϵ''	$\tan\delta$
0	9.279122	1975.35	79.06	13.50	0.1708
25	9.279017	2038.58	80.88	12.24	0.1513
65	9.279048	2039.20	80.31	12.23	0.1522
89	9.279097	2035.65	79.50	12.29	0.1547
107	9.279066	2071.78	80.03	11.64	0.1454

Table 9.17: Microwave data for 0.23 ratio of the reaction system at 915 MHz.

Hours	f_s	Q_s	ϵ'	ϵ''	$\tan\delta$
0	9.278920	2103.05	82.56	11.03	0.1337
25	9.278987	2131.81	81.41	10.51	0.1292
65	9.279031	2117.96	80.65	10.76	0.1334
89	9.279108	2147.25	79.29	10.24	0.1292
107	9.279085	2110.53	79.71	10.89	0.1367

As seen from the data in the tables 9.13-9.17, the variation in microwave data at 915 MHz is also dependent on the reaction time and the ratio of the reactants. Similar to the results observed at 2450 MHz, there is no relationship between the microwave data with time at the specific ratio except at higher ratio reactants (or higher concentration of the reactants in this case) (Table 9.18). Relationships between loss factor (ϵ'') vs ratio (c) and loss tangent ($\tan\delta$) vs ratio (c) were also obtained (Table 9.19). The reason for this observation is the same as that observed at 2450 MHz.

Table 9.18: Regression equation constants and coefficients of determination (R^2) of the equations for the Maillard reaction model system consisting of glucose and lysine in water with time (hours) for different ratios at 915 MHz.

Ratio	Dielectric loss factor			R ²	Loss tangent			R ²
	a ₅ × t ² + b ₅ × t + c ₅				a ₆ × t ² + b ₆ × t + c ₆			
	a ₅	b ₅	c ₅		a ₆	b ₆	c ₆	
0.71	0.0007	-0.0685	17.9989	0.8421	0.000010	-0.000879	0.22163	0.8582
0.54	0.0005	-0.0636	16.3434	0.7258	0.000006	-0.000683	0.19947	0.5908
0.42	0.00009	0	12.5961	0.7110	0.000001	0	0.15571	0.6881
0.37	0.0001	-0.0261	13.2641	0.7035	0.000002	-0.000408	0.16715	0.6078
0.23	0.0001	-0.0172	10.9881	0.3448	2.7E-7	0	0.13113	0.1086

Table 9.19: Equation constants and coefficients of determination (R^2) of the equations for the Maillard reaction model system consisting of glucose and lysine in water with ratio at the tested time at 915 MHz.

Time	Dielectric loss factor			R ²	Loss tangent			R ²
	a ₇ × c ² + b ₇ × c + c ₇				a ₈ × c ² + b ₈ × c + c ₈			
	a ₇	b ₇	c ₇		a ₈	b ₈	c ₈	
0	0	14.7010	7.7156	0.9342	0	0.17808	0.09732	0.9193
25	0	13.098	7.4242	0.9948	0	0.15853	0.09260	0.9963
65	0	14.043	7.2266	0.9892	0	0.17373	0.08992	0.9859
89	0	14.6152	6.8373	0.9964	0	0.17764	0.08769	0.9924
107	-20.515	0	9.4966	0.9784	0.2583	0	0.11810	0.9799

Similarly, in order to better describe the variation of dielectric loss factor and loss tangent for varying reaction mixtures tested at 915 MHz, the SAS analysis was performed on the data. Relationships among dielectric loss factor, loss tangent, ratio of the reactants and reaction time at room temperature were established as shown below:

$$\varepsilon'' = 3.84 \times 10^{-4} t^2 + 0.04tc - 0.06t + 13.01c + 8.45 \quad (R^2=0.9517) \quad (9.3)$$

$$\tan \delta = 5.07 \times 10^{-6} t^2 + 5.64 \times 10^{-4} tc - 7.88 \times 10^{-4} t + 0.16c + 0.11 \quad (R^2=0.9445) \quad (9.4)$$

Both equations obtained were also found to be very significant at 0.0001 level. Therefore, it is also possible to use microwave data at 915 MHz to study the kinetics of this type of chemical reaction when the appropriate system is chosen.

9.5 Conclusions

The relation of dielectric properties for the Maillard reaction model systems with reaction time and reaction ratio was established through the measurement and SAS analysis. It is also possible to use loss factor or loss tangent at both frequencies to describe the kinetics of this type of Maillard reaction models system when the reactants has higher ratio (or higher concentration of the reactants in this case).

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CONNECTING TEXT

In Chapters III–VII, we identified mathematical relationship between dielectric properties of solutions and their concentrations or temperatures. The application of those results for chemical reactions was demonstrated in Chapters VIII and IX. In the following two chapters, the advantages of using microwave technology and the reason for microwave assisted chemical reactions will be presented.

In Chapter X, microwave-assisted esterification reaction is demonstrated.

The material presented in this chapter has been published in a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2002. A novel way to prepare n-butylparaben under microwave irradiation. *Tetrahedron letters*, 43(1): 45-48.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

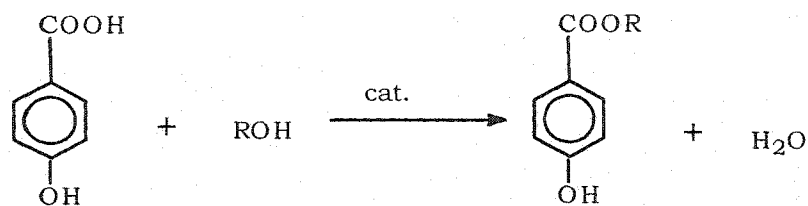
X. A NOVEL WAY TO PREPARE *n*-BUTYLPARABEN UNDER MICROWAVE IRRADIATION

10.1 Abstract

The synthesis of *n*-butylparaben under microwave irradiation in the presence of an inorganic salt ZnCl_2 as a catalyst is reported. Using this specific catalyst for the synthesis of the *n*-butylparaben under microwave irradiation, not only shortens the reaction time, but also reduces the pollution from the use of concentrated sulfuric acid and prevents the complicated after-treatment handling problems. The reason for this type of microwave-assisted reaction is also demonstrated from the temperature profiles of the reaction. The ratio of the reactants for the better microwave energy efficiency is discussed. The use of microwave irradiation for the large-scale production of this type of food preservative is therefore feasible.

10.2 Introduction

p-Hydroxybenzoic acid esters (parabens) have been widely used as antimicrobial preservative agents in food, drugs and cosmetics for more than fifty years due to their broad antimicrobial spectrum (Soni et al., 2001). Parabens are very versatile in terms of food preservatives, differing from the other preservatives such as benzoates, propionates, and sorbates, because they are not weak acid compounds but have wide pH range. The antimicrobial activity of parabens is directly dependent on the chain length (Robach, 1980; Dziezak, 1986). For example, the ability of *n*-butylparaben to inhibit bacteria is 4 times as that of ethylparaben (Zhang et al., 1998). The increasing use of these types of compounds with relatively low toxicity, good stability, non-volatility and non-irritability in those fields has led to the development of many techniques for the synthesis and assay these compounds. In general, most methods of the paraben syntheses involve the presence of catalyst such as concentrated sulfuric acid and PTSA (*p*-toluene sulfonic acid). In most cases, large excess of either acid or alcohol is used in the condensation to give a higher yield of the desirable esters (Scheme 10.1).



Scheme 10.1. The synthesis of parabens
(cat. = catalyst such as PTSA, H₂SO₄)

However, these methods have limitations of general applicability owing to low yields, extensive by-product formation and harsh reaction conditions. In fact, the use of large amounts of condensing reagents and activators should be avoided in order to promote green agricultural food engineering and efficient energy consumption. The direct condensation of acids with alcohols using small amount of catalyst under microwave irradiation is the most suitable method.

The use of microwave irradiation techniques has profound impact on the solution of the synthesis of this type of compounds. Since the appearance of the first papers on the application of microwave for organic synthesis (Gedye et al., 1986; Giguere et al., 1986), numerous papers regarding the application of this special technology in organic synthesis have been published [website: <http://www.ang.kfunigraz.ac.at/~kappeco/microlibrary.htm> (a lot of references were given on this home page)]. The use of microwave in the synthesis results in better selectivity, rate enhancement, and reduction of thermal degradation and higher energy consumption efficiency when compared to traditional heating. In addition, microwave assisted synthesis without surplus reactant offers such advantages as the reduction of hazardous explosions and the removal of excess reactants or high boiling solvents from the reaction mixture. Esterification of carboxylic acid in the presence of catalysts such as concentrated sulfuric acid and PTSA by employing microwave energy has been extensively investigated (Majetich and Wheless, 1997; Majetich and Hicks, 1995; Loupy et al., 1993). Further, microwave irradiation has also been utilized for the synthesis of parabens using catalysts such as concentrated sulfuric acid, PTSA and inorganic acid. Liu et al. (1999) reported that butyl *p*-hydroxybenzoate was synthesized under microwave irradiation by the esterification of *p*-hydroxybenzoic

acid with *n*-butanol using phosphotungstic acid as a catalyst. Chen et al. (1993) reported that *p*-hydroxybenzoic acid was refluxed with ROH (R=Et, *n*-Pr, Bu) employing concentrated sulfuric acid as a catalyst under microwave irradiation for 30 minutes to give 85.1-86.5% corresponding esters. However, after checking Scifinder Scholar provided by CAS (Chemical abstract service), to our best knowledge, there is no literature relevant to the use of ZnCl₂ as a catalyst to perform the esterification under microwave irradiation. In this report we describe a fast microwave-induced synthesis of potentially practical use in the chemical engineering by esterification of alcohol with *p*-hydroxybenzoic acid in the presence of an inorganic salt ZnCl₂ as a catalyst. The results are compared with the traditional synthesis. It not only can save the reaction time, but also can reduce the pollution associated with the use of concentrated sulfuric acid and avoid the complicated after-treatment handling problems. Although the reason for microwave assisted chemical reaction has been extensively investigated, most results contributed to "hot spot" or "localized superheating" of the solvent (Gedye and Wei, 1998; Westaway and Gedye, 1995; Hoopes et al., 1991). In addition, materials or components of a reaction mixture can differ in their ability to absorb microwaves. Differential absorption of microwaves will lead to differential heating and localized thermal inhomogeneities that can't be duplicated by conventional heating techniques. It also results in "microwave effects". In our paper, the reason for this microwave assisted chemical reaction is discussed by making use of temperature data of the reaction mixture during the microwave processing.

10.3 Materials & Methods

10.3.1 Materials

The following chemicals: *n*-butanol, methylparaben, *n*-butylparaben, *p*-hydroxybenzoic acid, PTSA, and ZnCl₂ were purchased from the Sigma-Aldrich Canada (Ontario). All reagents and catalysts were used without further treatment.

10.3.2 Experimental procedure

Reactions have been carried out by employing a Synthrowave S402 with a mono-mode MW cavity from Prolabo operating at 2450 MHz with power range of 0-300W in a tubular quartz reactor (250-ml) with irradiation being monitored by a PC. The temperature of reaction media was measured continuously with an IR-pyrometer, which was an integral part of the Synthrowave 402. For the sake of comparison, reactions were also carried out using traditional heating in the presence of ZnCl_2 as a catalyst and reactions were also performed using PTSA as a catalyst in the presence of microwave or conventional heating.

10.3.2.1 General procedure 1 (Microwave assisted synthesis):

A mixture of 8 ml of butanol, 0.18 g ZnCl_2 and 1.72 g *p*-hydroxybenzoic acid was introduced together in the quartz reactor of the synthrowave 402 apparatus equipped with a condenser. The irradiation was carried out in the following sequence at 70% power (300 W * 70%): 15 s off, 30 s on; 15 s off, 30 s on; 15 s off, 30 s on; 30 s off, 30 s on; 15 s off, 30 s on. After heating and cooling, the mixture was diluted by ethanol and analyzed by GC. Methylparaben was used as internal standard to calibrate the yield of reaction.

10.3.2.2 General procedure 2 (Conventional heating method):

A mixture of 3.46 g of *p*-hydroxybenzoic acid and 0.35g ZnCl_2 was introduced to 250 ml reaction flask and then 16 ml of butanol was added. The mixture was refluxed on a hotplate for 45 minutes. After heating and cooling, the product was analyzed as above.

10.3.2.3 GC analysis:

The GC was operated with an injector temperature of 250 °C and a helium carrier gas flow rate of 24 ml/min. The GC column was a non-polar general-purpose capillary column [30 m × 0.25 mm i.d., 0.25-micron thickness, Phase DB5 (Catalogue No. 122-5032, J&W Scientific Co.)]. The detector (FID) was operated at 250 °C and oven temperature was programmed as follows:

1) Initial temperature was 100 °C; 2) Level 1, 5.0 °C/min, 100 °C, keep 2 min; 3) Level 2, 10 °C/min, 160 °C, keep 5 min; 4) Level 3, 10 °C/min, 250 °C, keep 5 min.

The products were identified by comparison of their GC retention time with those of authentic samples. The yields were calculated from the theoretical standard calibration line.

10.4 Results & Discussion

10.4.1 The calibration line

The responses of the yields to GC detector were found to be linear (Figure 10.1) to the ratio of the peak areas of butylparaben (PB(A)) to the peak area of methylparaben (PM(A)).

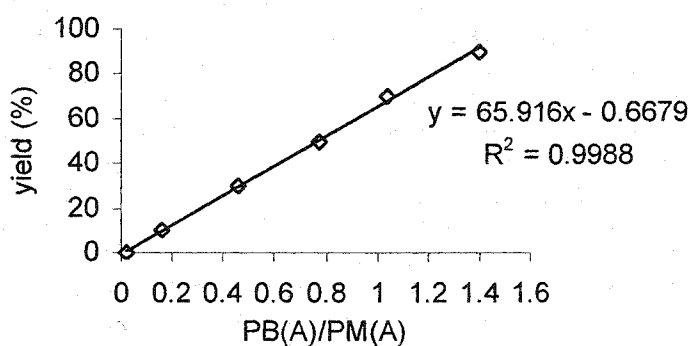


Figure 10.1: Theoretical calibration line of paraben.

(yield = number of mole for ester after reaction / number of mole for acid before reaction)

10.4.2 Reactions under conventional heating

As expected, the butylparaben was successfully synthesized using PTSA as a catalyst by the conventional heating method with a yield of 76%. However, when PTSA was replaced with ZnCl_2 as a catalyst under the same reaction conditions, the yield was reduced to a meager 3.5% of the original reaction. The results are shown in Table 10.1.

10.4.3 Reactions under microwave irradiation

As expected, the butylparaben was successfully synthesized using PTSA as a catalyst under microwave irradiation. However, the yield was lower than the conventional method due to the much short reaction time. Interestingly, the yield for the use of ZnCl_2 was slightly higher than that of the reaction catalyzed by PTSA. The results are also shown in Table 10.1.

Table 10.1: Esterification of parahydroxybenzoic acid and n-butanol under microwave irradiation and classic heating.

Entry	Catalyst	heating mode	yield (%)
1		Microwave irradiation	0
2		Conventional heating	0
3	PTSA	Microwave irradiation	41
4	ZnCl_2	Microwave irradiation	43
5	PTSA	Conventional heating	76
6	ZnCl_2	Conventional heating	3.5

10.4.4 Temperature profiles of the reaction

The temperature profiles of the esterification of butanol and *p*-hydroxybenzoic acid in the presence of PTSA or ZnCl_2 under microwave irradiation are shown in Figures 10.2 and 10.3 respectively.

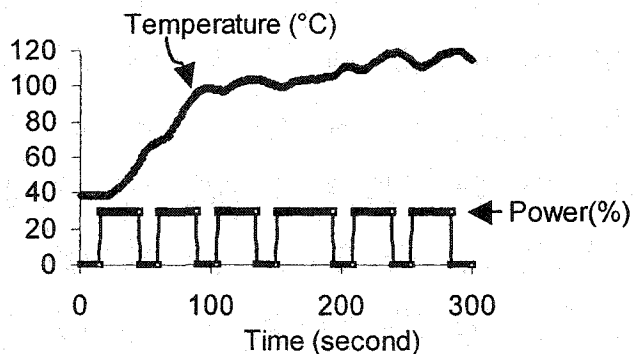


Figure 10.2: Temperature (°C) profile of esterification under microwave irradiation in the presence of PTSA.

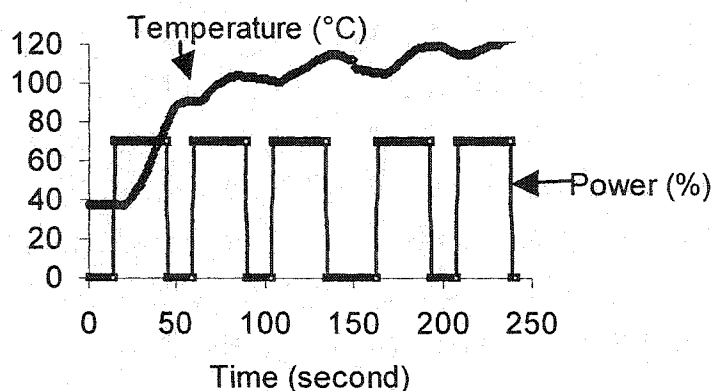


Figure 10.3: Temperature (°C) profile of esterification under microwave irradiation in the presence of ZnCl_2 .

As can be seen, the temperature under microwave irradiation was slightly higher than the boiling point of butanol (117.6°C). This is in accordance with the previous report by Baghurst and Mingos (1992) and Hoopes et al. (1991). This results in reaction rate enhancement when compared with the synthesis by using classic heating. In classic heating, the temperature provided for the reaction is usually the reflux temperature. The temperature in the case of ZnCl_2 as a catalyst was also slightly higher than the boiling point of butanol. This not only can explain rate enhancement under microwave irradiation, but also can give an explanation for the reason that the desired product could not be successfully produced under conventional heating. According to this, it is important to point out that each catalyst has its exact reaction temperature whether the reaction is performed using microwave heating or conventional heating. The non-thermal effect claimed by some authors probably result from difficulties in relating to temperature distribution estimation and keeping the absolutely identical reaction conditions while comparing.

10.4.5 Effect of microwave parameters

In order to optimize the reaction conditions, a series of experiments in the reactor were performed. Figure 10.4 shows the effect of the irradiation power supplied and the ratio of the reactants on the yield of esterification.

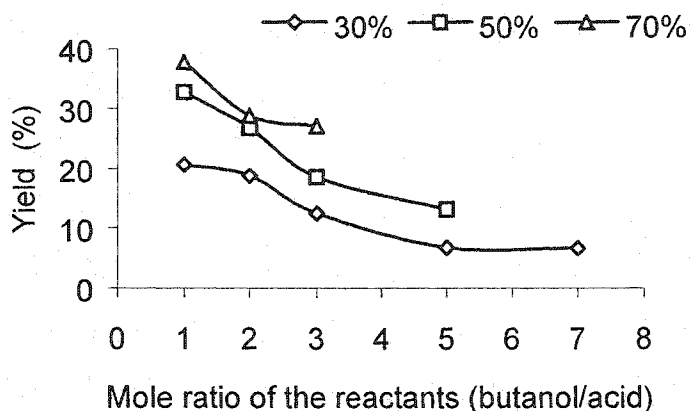


Figure 10.4: Effect of microwave irradiation power supplied (%) and the ratio of the reactants (mole ratio = butanol/acid) on the yield of esterification.

As can be seen, an increase in the irradiation power provides an increase in the yield of butylparaben. Interestingly, the yield decreases with an increase in the ratio of the reactants. For example, the higher yield was obtained when the reactant ratio was 1:1. This result is different from the traditional concept that large excess of either acid or alcohol is used in the condensation to give a higher yield of the desirable esters.

10.5 Conclusions

This paper described a microwave-assisted synthesis of *n*-butylparaben in the presence of ZnCl_2 as a catalyst and identified the reason for the difference between the reaction performed under microwave heating and conventional heating. In direct esterification, the catalytic use of inorganic salts is practical and economical because of its simplicity and applicability to large-sale operations and at the same time avoiding the higher cost of PTSA or the use of concentrated sulfuric acid. Also, this procedure gave the right ratio of reactant, which should be 1:1. With this ratio, the microwave energy efficiency is the highest. Further optimisation of the irradiation time, microwave power supplied will be investigated in order to make this microwave technology applicable in agriculture and food industry.

Acknowledgment

We are grateful for financial support from CIDA (Canada international development agency), NSERC and FCAR funding.

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CONNECTING TEXT

In microwave-assisted esterification (Chapter X), a new catalyst was reported to be useful for esterification of para-hydroxybenzoic acid with 1-butanol under microwave irradiation. In Chapter XI, Maillard reaction under microwave irradiation was studied in absence of a solvent. The advantage of the use of microwave irradiation in this reaction will be also demonstrated.

In this chapter microwave assisted Maillard reaction model system without solvent is presented.

The material presented in this chapter will be submitted for publication in a peer-reviewed journal (see details of publication below).

Liao, X., Raghavan, G. S. V., and Yaylayan, V. A. 2002. Microwave Assisted Solvent-free Maillard Reaction Model System Consisting of Glucose and Lysine, *Tetrahedron (to be submitted)*.

The contributions made by different authors are as follows: (i) The first author is the Ph.D. student who performed the experimental work and wrote the manuscript, (ii) the second and third authors are the student's co-supervisors who contributed in all aspects of the project.

XI. MICROWAVE ASSISTED SOLVENT-FREE MAILLARD REACTION MODEL SYSTEM CONSISTING OF GLUCOSE AND LYSINE

11.1 Abstract

A Maillard reaction model system consisting of glucose and lysine under microwave irradiation was investigated. The dielectric properties of the chemical reaction, absorbance at 287 nm and 420 nm and colour development are reported. The result of this solvent-free reaction is a novel method since it is completely dry compared to the earlier concept of solvent-free microwave reaction needing at least one liquid reactant.

11.2 Introduction

The Maillard reaction, non-enzymatic browning, is actually a complex set of reactions that takes place between amines, usually from proteins and carbonyl compounds, generally sugars, especially glucose, fructose, maltose or lactose. The Maillard reaction has far reaching implications in the production of flavours and aromas, nutrition, toxicology, and technology in food processing (Ikan, 1996; Yaylayan, 1997). In fact, foods prepared in microwave oven usually generate less desirable flavours and browning colours than those prepared by a conventional method due to their heat distribution characteristics (temperature profiles). The higher temperature of the surroundings in a conventional oven causes the Maillard reaction, resulting in surface browning and production of desirable flavours in foodstuffs. Similar browning and flavour production, however, do not take place in foodstuffs prepared by microwave ovens mainly because of the lower temperature of the surroundings of the foodstuffs. However, flavour researchers have made efforts to solve these problems by modifying the food formulations, adding flavour precursors, using special package materials and so on (Yu et al., 1998). In general, the use of microwave irradiation in food engineering and organic chemistry will be promising due to the advantages over the traditional heating methods such as the fast heating rate, timesaving and good quality of product and

selectivity (Decareau, 1985). Some studies about Maillard reaction under microwave irradiation have been studied. A recent review has been written by Yaylayan (1996). Those studies emphasise the influence of various pH values, moisture content, irradiation time, the ratio of sugar and acid, electrolytes on the reaction under microwave irradiation (Zamora et al., 1992). Most of them observed that there were some differences between microwave heating and conventional heating. As we know, the successful application of microwaves is directly associated with the dielectric properties of the materials. These properties are defined in terms of dielectric constant (ϵ') and loss factor (ϵ''). The former is a measure of the ability of a material to couple with microwave energy and the latter is a measure of the ability of a material to dissipate electric energy, converting it into heat. However, those studies of microwave assisted Maillard reaction did not associate the differences from microwave heating with the dielectric properties of the reactants and were performed in the presence of solvent such as water.

Recently, a solvent-free synthesis under microwave irradiation has been advocated and developed due to its advantage of avoiding the use of large volumes of solvent. There are several advantages to this concept; reduction of solvent emissions, scale-up advantage, and higher safety due to the reduction of the risk of overpressure and explosions (Loupy et al., 1993 and 1998; Strauss, 1999). However, Vidal et al. (2000) concluded that reactions between solids might not take place and need the use of a high boiling point solvent after they re-examined the microwave-induced synthesis of phthalimides. This conclusion prompted us to study the chemical reactions between two solids under microwave irradiation. In addition, we attempted to establish some basic understanding of the relationships about the dielectric properties, colour development after reaction under microwave heating and conventional heating. The Maillard model system, consisting of D-glucose and L-lysine, is used in this investigation.

11.3 Materials & Methods

11.3.1 Materials

D-glucose (ACS reagent) was purchased from the Sigma Chemical Co. (Ontario, Canada) and L-lysine (97%) was obtained from Aldrich Chemical Co. (USA). They were used without further purification.

11.3.2 Reaction procedures

(1) Microwave heating procedure

0.4 g glucose and 0.4 g lysine were introduced to a 5-ml capped bottle. They were mixed together through magnetic stirrer and then exposed to microwaves to reach the specific final temperature by using Fiso Microwave workstation (Figure 11.1). The Microwave workstation consists of a microwave oven with an electronic interface, a fiber-optic slip-ring for temperature and pressure measurements.

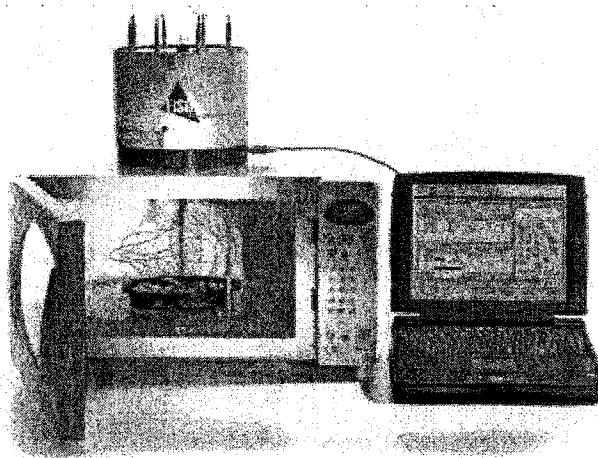


Figure 11.1: Fiso Microwave workstation.

(2) Conventional heating procedure

0.4 g glucose and 0.4 g lysine were mixed together and then were introduced to a 5-ml capped bottle. The mixture was heated by a hotplate to around 65°C and then cooled to room temperature.

11.3.3 Dielectric properties measurement

After heating both systems, 4-ml water was added to dissolve the mixture. Using a cavity perturbation technique, the dielectric properties of the solutions were measured at 2450 and 915 MHz. The measurement required a dielectric analyser (Gautel Inc.), a PC, measurement cavity. The system software calculated the dielectric parameters from the cavity Q factor, transmission factor (ΔT , the changes in the cavity transmission), and the

shift of resonant frequency (ΔF). Before starting measurements, the calibration was verified by taking measurements on a standard liquid (water) of known dielectric properties.

11.3.4 Colour development measurement

After heating, 4-ml water was added to dissolve the mixture. Six millilitres of water was added to the 0.4 ml of the above solution and then the diluted solutions was subjected to colour measurement. Colour was measured in CIELAB space by using a Chroma Meter (Minolta Chroma Meter, CR-200b, Minolta Camera Co. Ltd., Azuchi-Machi, Chuo-Ku, Osaka 541, Japan). The samples were placed inside a sample holder for colorimetric assessment of the reaction mixture. The Chroma Meter was calibrated against a standard calibration plate of a white surface with L^* , a^* and b^* value according to the recommendations from manufacture. The measurements were repeated three times for each sample. Data are reported as L^* , uniform lightness and the chromaticness coordinates a^* (+ red to - green) and b^* (+yellow to - blue).

11.3.5 Absorbance measurement

Absorbance was measured in a 1-cm quartz cell in a Spectrophotometer from 200-700 nm. The distilled water was used as background. The solution was the same as the diluted solution, which was subjected to colour measurement.

11.4 Results & Discussion

11.4.1 Microwave heating profiles

A representative microwave heating profile is shown in Figure 11.2. Microwave heating rate is affected by the microwave power provided. As seen from Figure 11.2, for higher microwave powers, faster microwave heating was achieved.

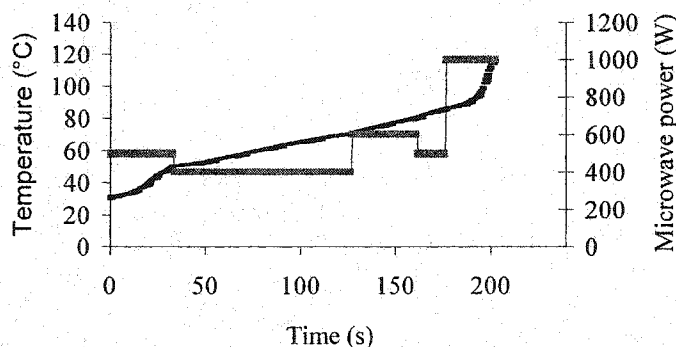


Figure 11.2: Microwave heating profile at various microwave powers supplied:

(--): microwave power; (—): temperature.

11.4.2 Absorbance at 420 nm and 287 nm

The absorbance at 420 nm and 287 nm for the reaction mixtures after microwave irradiation or conventional heating is shown in Table 11.1. The trends for absorption at both wavelengths were almost the same. The changes in absorbance at both wavelengths for the conventional heating without solvent (water) are much smaller than that with solvent under the same reaction conditions. Therefore, heat transfer through solvent is one of the important factors in the conventional heating. It can increase the frequencies of the collision of the reactants and is helpful in the progressing of the reaction. For the microwave heating, even without the addition of a solvent (water) in the system, the chemical reaction still took place as long as microwave heating provided high enough temperature as shown in Table 11.1. It may take the advantages of the volumetric heating produced by microwave to drive the chemical reaction. The changes in absorbance are also associated with the microwave power supplied (Table 11.1).

11.4.3 Colour development

CIELAB lightness (L^*) and chrom (a^* , b^*) of colour development are given in Table 11.1. The effect of microwave power supplied or temperature on the colour development is also observed.

Table 11.1: Absorbance and color development of Maillard reaction.

Trials	Heating methods	Final temperature (°C)	Heating time (Second)	A _{287nm}	A _{420nm}	L*	a*	b*
1	No heating	25		0.043	0.006	98.65	-0.32	2.37
2	Conventional heating	65	3600	0.218	0.044	103.10	-0.76	5.51
3	Conventional heating*	65	1800	2.102	0.357	100.59	0.73	14.30
4	MW 500 w	66	69	There was no color development observed				
5	MW 500 w	96	140	0.712	0.155	100.11	-1.72	12.16
6	Microwave**	115	**	3.143	0.920	90.18	5.41	9.86
7	MW 1000 w	139	68	2.985	0.804	96.22	4.06	10.38

*: 4-ml water was added to the system before heating.

** : The microwave heating procedure was: 500w 33s; 400w 93s; 600w 35s; 500w 15s, 1000w 26s. (Total microwave irradiation time is 176s)

11.4.4 Changes in dielectric properties

For this specific Maillard reaction model system, there were some changes in the dielectric properties between before and after reaction (Table 11.2). The dielectric constant at 2450 MHz increases after reaction, while at 915 MHz it decreases. The higher final reaction temperature was attributable to the higher decrease or increase in dielectric constant as observed in the experiments. The loss factor at both frequencies decreased after reaction. Interestingly, there was no major difference in loss factor at both frequencies (Table 11.2).

Table 11.2: Dielectric properties before and after reaction.

Trial	Final temperature (°C)	Dielectric constant		Loss factor	
		2450 MHz	915 MHz	2450 MHz	915 MHz
1*	25	64.79	69.60	22.05	21.69
5	96	65.50	69.10	21.21	20.7
6	115	66.40	67.84	18.15	18.05
7	139	67.11	67.49	17.63	16.69

*: before reaction, no heating was provided in this system.

11.5 Conclusions

The Maillard reaction model system consisting of glucose and lysine was investigated under microwave heating and conventional heating. For the conventional heating, it is important to add water to make them homogeneous to make the reaction happen faster. While for the microwave heating, even without the addition of solvent (water), the reaction can take place quickly if the temperature provided by microwave is high enough.

Acknowledgement

We thank CIDA (Canadian International Development Agency), NSERC, and FCAR for their financial support. Fiso Inc is also appreciated for their involvement in providing the Microwave workstation.

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XII. GENERAL SUMMARY AND CONCLUSIONS

12.1 General Summary and Conclusions

In many cases, the temperature provides the driving force for chemical reactions. Microwave heating is a potential and practicable heating method, which can bring a clean friendly environment. Since the advent of the first papers about the application of microwave heating in organic chemistry, numerous papers have been presented in the peer-reviewed journals. This technology not only encourages scientists to do further research not just in the labs, but take it to the industrial applications. However, awareness about the dielectric properties of the materials is very important due to the fact that microwave heating is directly associated with them.

The main goal of this project was to obtain the dielectric properties of the chemicals at microwave frequencies of 2450 and 915 MHz and the application of dielectric properties in the chemical reactions. More specifically, the objectives of this study were to measure the dielectric properties of the alcohols, glucose aqueous solutions, and lysine aqueous solutions, esterification and Maillard reaction model systems, establish the predictive models and demonstrate the advantages of the use of microwave irradiation in the organic chemical reactions.

To meet these objectives, experimentation started with all the chemicals mentioned earlier. The cavity perturbation technique was employed in the measurement of the dielectric properties. Microwave assisted dissolution was presented. The data obtained were analyzed by SAS Program. The reactions under microwave irradiation were studied from the temperature profile during the microwave process.

Through the measurement and theoretical analysis, it was learnt that dielectric properties of the materials depended on the material variety, concentration of component, temperature and the microwave frequencies applied.

Through the SAS analysis, it was possible to develop models to predict dielectric properties of material with the key independent variables such as concentration, temperature or both.

Through the study of two type of microwave assisted chemical reactions, it showed the advantages of employing microwave in the chemical reaction such as heating fast, shortening the reaction time, providing the distinctive temperature distribution.

Through this study, it was possible to demonstrate that chemical reaction outcome can be linked to dielectric properties which is more of a physical attribute of the material.

Main conclusions are recapitulated as follows:

- i) At 2450 and 915 MHz, dielectric constants of all alcohols tested increase with temperature. Contrary to dielectric constant, the loss factors of methanol decreased with temperature, while the other alcohols tested, except ethanol, first increased and then decreased with temperature.
- ii) The dielectric constant of supersaturated α -D-glucose solutions at 2450 MHz increased with temperature, but generally decreased with concentration. The dielectric loss factor decreased with temperature, but generally increased slightly with concentration. At temperatures tested, at least two concentrations showed nearly identical values of dielectric constant or dielectric loss factor.
- iii) At 2450 MHz and 915 MHz, dielectric properties of α -D-glucose solutions were shown to be dependent on the temperature and concentration.
- iv) At 2450 MHz, dielectric properties of lysine solution were shown to be dependent on the concentration.
- v) The dielectric properties of esterification reaction model systems were investigated with respect to the theoretical yields. It is possible to correlate the Q factor or loss factor with the yield of the reaction by measuring the dielectric properties of the reaction.
- vi) The dielectric properties of Maillard reaction model system were measured at both 2450 and 915 MHz and analyzed using SAS. It is also possible to use loss factor or loss tangent at both frequencies to describe the kinetics of this type of reactions when the reaction mixture is concentrated.
- vii) The predictive models regarding dielectric properties were developed.
- viii) A microwave-assisted synthesis of butylparaben in the presence of ZnCl_2 as a catalyst was described. The procedure gave the right ratio of reactant,

which should be 1:1. With this ratio, the microwave energy efficiency is the highest.

- ix) The Maillard reaction model system consisting of glucose and lysine was investigated under microwave heating and conventional heating. For the conventional heating, it is important to add a solvent (water) to make a homogeneous solution for achieving the desired reaction. While for the microwave heating, even without solvent, the reaction can take place as long as the temperature provided by microwave is high enough.

12.2 Contributions to knowledge

The major contributions to knowledge are:

1. The models for dielectric properties of the chemicals such as alcohols, glucose aqueous solution, and lysine aqueous solution were established at two industrial frequencies.
2. A relationship between the dielectric properties and chemical reaction yields was developed. It was possible to use dielectric loss factor to monitor the yield of the mimicked esterification reaction.
3. Through correlations of dielectric properties with the reaction time and the concentration of the component of the chemical reaction, the kinetics of the chemical reaction was studied.
4. Using microwave technology, a novel way to prepare one type of food preservatives and solvent free Maillard reaction were achieved.
5. The reason for microwave assisted esterification from the temperature file and microwave assisted solvent free Maillard reaction was demonstrated. Temperature provided is really a crucial factor for chemical reaction whether it is performed by conventional heating or microwave irradiation.

12.3 Recommendations for future research

This study was performed with an aim to obtain dielectric properties of the chemicals and chemical reaction at microwave frequencies of 2450 and 915 MHz.

Models were developed to correlate dielectric properties with the temperature, concentration, reaction time, and yield. The applications of dielectric properties to chemical reactions were also studied. Since microwave heating is linked to the dielectric properties of the materials and it provides the distinctive temperature distribution during the heating process, the encouraging results in this study suggest that the research in future should be pursued as follows:

- i) Study the temperature profile of those alcohols during the microwave heating at 2450 or 915 MHz thus correlating the microwave-heating model with the dielectric properties at both frequencies. It will give more guidance in the selection of solvent for the microwave assisted chemical reaction and extraction.
- ii) Since it is possible to monitor the yield of the mimicked esterification reaction, more experiments are needed to find ways to scale-up the system.
- iii) Further investigations are necessary to study the chemical reaction from the point of loss factor.
- iv) Design an automatic system (probably flow through system) to measure and analyze dielectric data.
- v) Design a microwave-chemical sensor to determine the process of the chemical reaction.

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