Broadband Dielectric Properties of Honey: Effect of Water Content

M. Yang, Y. Gao, Y. Liu, X. Fan, K. Zhao*, and Sh. Zhao**

ABSTRACT

Influence of water on the dielectric properties of jujube, yellow-locust, and vitex honey was investigated by dielectric spectroscopy in broadband from 40 Hz-40 GHz. At lower frequencies, two relaxations which were from interface polarization and dipole orientation polarization of macromolecules in honey were observed. Other relaxations contributed by free and bound water were observed at microwave frequencies. The analysis of the observed relaxations revealed that the honey/water interface and bound water molecules that interact with the macromolecules in honey are responsible for the changed dielectric properties of honey solutions. Besides, the linear correlations between the permittivity (around 2.45 GHz) and water content of honey solutions were developed, which indicates that water content in honey solutions can be measured by dielectric spectroscopy. In addition, we also compared the dielectric properties of different pure honey types and found that the pure yellow-locust honey, which contains the maximum water content, has the highest permittivity. This suggests that different honey types with different water content can be roughly identified by dielectric spectroscopy. This study shows that the water content influences the dielectric properties of honey and dielectric spectroscopy is feasible for detecting honey adulteration with water.

Keywords: Honey adulteration, Permittivity, Relaxation.

INTRODUCTION

Honey is a natural sweetening agent that is rich in sugars, organic acids and various amino acids (Turhan et al., 2008), and has significant nutritional benefits. The water content in honey is one of the major indicators that affect the keeping quality, storability or crystallization of honey (Lazaridou, et al. 2004). According to the (Codex Alimentarius Standards) and (EU Council Directive), the water content for pure, natural honey should be under 20% because high amounts of water will reduce the nutritional value. Besides, higher water content also makes the glucose and fructose in honey ferment easily, which produces lactic acid and alcohol (Camara, and Laux, 2010) and reduces the shelf-life and nutritional value. However, for the economic benefit, honey adulterated with water by beekeepers or honey manufacturers is common in the market. Thus, determination of water content in honey has become one of the most widely studied factors.

At present, the water content in honey is usually estimated by hand-held refractometer or an Abbe-type refractometer, but the former is limited by accuracy and the latter is easily influenced by temperature. So, it is necessary to develop a more useful tool to determine the water content for honey. Dielectric spectroscopy, which is sensitive to molecular polarity, has been widely used to characterize various foods just as recently reviewed by (El Khaled et al. 2016). In particular, because dielectric spectroscopy is sensitive to water molecules

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685
(Angulo-Sherman, and Mercado-UrIBE, 2011) it has been used as a simple, rapid, and non-destructive measuring technique (Toyoda, 2003) to determine moisture content of food. (Afzal et al. 2010) once determined the water content by measuring the permittivity of leaves in crops. (Traffano-Schiffo et al. 2015) found that there was a direct relationship between the dielectric loss and the number of water molecules on the surface of meat during the drying process at 20 GHz. Besides, the relationship between water content and dielectric properties of pineapple has been reported by (Barba and Lamberti, 2013). Moreover, research proved that it’s feasible to predict the water content in honey using dielectric spectroscopy. For example, (Ahmed et al. 2007) reported the dielectric properties of several Indian pure honey types in the frequency range of 900 to 2550 MHz and found that water content and electrical conductivity of honey were positively correlated. (Puranik et al., 1991) found that the dielectric loss of honey was increased with water. (Guo et al., 2010) developed the linear correlations between permittivity and the total soluble solids and water contents, and the correlation between the conductivity and water contents of honey. (Guo et al., 2011). Although the relation between the dielectric properties and water content of honey solutions have been studied, the report about the essential reason of the influence of water on the dielectric properties of honey is relatively few. Knowledge of the essential reason about the influence of water on the dielectric property of honey is necessary, because dielectric property is closely related to many other properties of honey, such as rheology and viscosity, which are very important for its storage and handling procedures (Dobre et al., 2012 and Assil et al., 1991).

The objective of this study was to investigate the influence of water content on the dielectric properties of honey in a broadband frequency, and to develop the relationship between the water content and dielectric properties of honey solutions. In particular, based on the observed dielectric relaxation, we expected to reveal the essential reason of the effect of water on the dielectric properties of honey from the microscopic point of view.

**MATERIALS AND METHODS**

**Honey Samples**

Jujube honey, yellow-locust flower honey and vitex honey were used in this study. The botanical origins were chosen because they are the most popular types produced and consumed in China. The samples were obtained from Yifeng Tang Ecological Bee Garden Co., Ltd, Xi’an, Shaanxi, China. All the samples were used in fresh state, and no crystals were present. The initial water content of the three honeys was supplied by the company from which we bought the honey. They were 180 (jujube honey), 190 (yellow-locust honey) and 180 mg g⁻¹ (vitex honey).

Predetermined amounts of deionized water were added to each pure honey, with 180, 190, and 180 mg g⁻¹ initial water contents in jujube, yellow-locust and vitex honey, to prepare honey-water solutions with different final water contents of 200, 350, 500, 700, and 900 mg g⁻¹ at room temperature. The masses were measured with an FA1004A Electronic Balance (Shanghai Liang Ping Instrument Co., Ltd., Shanghai, China) with precision of 0.0001 g.

**Dielectric Measurements**

Dielectric measurements were performed in the frequency range from 40 Hz to 40 GHz by Agilent E8363C PNA series network analyzer (Agilent Technologies, made in America, 10 MHz to 40 GHz) and 4294A precision impedance analyzer (Agilent Technologies, 40 Hz to 110 MHz) at the room temperature (25°C).

An Agilent 85070E open-ended coaxial probe was used for the dielectric
measurements by network analyzer. The permittivity $\varepsilon$ and dielectric loss $\varepsilon''$ were automatically calculated as functions of frequency by the built-in software of this measuring system, which was calibrated in accordance with the procedures recommended by the manufacturers.

A measurement cell with concentrically cylindrical platinum electrodes (Fang et al., 2010) was used for the measurements with the impedance analyzer. The raw data, Capacitance ($C_s$) and conductance ($G_s$), were corrected by the cell Constant ($C_l$), stray Capacitance ($C_r$) and residual inductance ($L_r$) (arising from terminal leads) based on the following equations 1 and 2 according to Schwan’s method (Schwan, 2013). The values of stray Capacitance ($C_r$), cell Constant ($C_l$) determined with three standard substances (pure water, ethanol and air) were 0.09 and 0.72 pF, respectively. The residual inductance ($L_r$) determined by KCl solution of varying concentrations is 2.29 nH.

$$C_s = \frac{C_s(1+\omega^2 L_c C_s) + L_g G_s^2}{1+\omega^2 L_c C_s}$$

$$G_s = \frac{G_s}{(1+\omega^2 L_c C_s)^2 + (\omega L_c G_s)^2}$$

Where, $\omega$ ($\omega = 2\pi f$, $f$ is the measurement frequency) is the angular frequency. Then, the permittivity $\varepsilon$ and conductivity $\kappa$ were determined by equations $\varepsilon = C_s/C_l$ and $\kappa = G_s\varepsilon_0/C_l$ ($\varepsilon_0$ is the permittivity of vacuum).

**Determination of Dielectric Parameters**

The dielectric parameters were obtained by fitting the following Cole-Cole equation to the experimental dielectric data. (Havriliak and Negami, 1967.)

$$\varepsilon^* = \epsilon_h + \sum \frac{\Delta\epsilon_i}{1 + (j\omega \tau_i)^\beta_i} + A\omega^{-m}$$

Where, $\epsilon_h$ is the high frequency limit of permittivity, $\Delta\epsilon_i$ is the strength of dielectric relaxation of the relaxation mode $i$, $f_j = -1$. $\tau_i$ (= $1/2\pi f_0 i$) being the characteristic relaxation frequency) is the relaxation time, and $\beta_i$ is the distribution parameter of the relaxation time of the relaxation numbered $i$. $A\omega^{-m}$ is the electrode polarization item.

**Figure 1.** The dielectric spectroscopy of jujube honey with different contents of water: Permittivity (A) and conductivity (B) spectra at radio frequency; permittivity (C) and dielectric loss (D) spectra at microwave frequency.
RESULTS AND DISCUSSION

Effect of Water Content on the Dielectric Properties of Honey

Figure 1 shows the dielectric spectroscopy of jujube honey solutions with different contents of water. The dielectric spectroscopy of yellow-locust and vitex honey is similar to jujube honey and is not listed here. Honey is a concentrated solution of sugars [fructose and glucose as the predominant monosaccharides (600–850 mg g\(^{-1}\)]](Doner, 1977) so, the permittivity of honey is smaller than water. Therefore, the permittivity of honey solutions increases significantly with the increase of water (Figures 1-A and -C). In addition, the permittivity spectra at radio frequency (Figure 1-A) shows that when the water content is less than 500 mg g\(^{-1}\), two significant relaxations located at around 10\(^5\) and 10\(^6\) Hz, called low-frequency and high-frequency relaxation, respectively, are observed. As the water increases, the gradually increased electrode polarization effect, owing to the increased conductivity of honey solutions, overshadows the relaxation phenomenon. This is also reflected by Figure 1-B: as the water content increases, the solution viscosity decreases and ion mobility increases, so, the conductivity of honey solution is increased. Figures 1-C and -D show that there exists a large dielectric relaxation related to the polarization of water molecules (Karásková et al. 2011) at microwave and, as the water increases, this relaxation gradually moves to higher frequencies, close to the relaxation of pure water. The above result indicates that the water content significantly affects the dielectric properties of honey in broadband.

To further explore the relation between the permittivity of honey solutions and water content, the permittivity of three honey solutions at around 2.45 GHz are taken to plot their dependence on water content. As shown in Figure 2, the two parameters show good linear correlations:

\[ \varepsilon = 0.0749 \, w_{\text{water}} + 2.32, \quad R^2 = 0.98 \] (Jujube honey) \hfill (4)
\[ \varepsilon = 0.0650 \, w_{\text{water}} + 10.66, \quad R^2 = 0.96 \] (Yellow-locust honey) \hfill (5)
\[ \varepsilon = 0.0731 \, w_{\text{water}} + 5.39, \quad R^2 = 0.98 \] (Vitex honey) \hfill (6)

If the permittivity of honey sample at 2.45 GHz is known, the water content can be calculated from these relationships. The honey could be regarded as adulterated honey if the calculated water content is higher than 200 mg g\(^{-1}\). This result shows that it is feasible to determine the adulterated honey with water and predict the water content in adulterated honey by dielectric spectroscopy.

Dielectric Analysis at 40 Hz to 110 MHz

To explore how the water influences the dielectric properties of honey, we fitted the
experimental permittivity curve of jujube honey solutions using Cole-Cole Equation (3) containing two relaxation modes, i.e., \( i=2 \) in Equation (3). Then, all the dielectric parameters in Equation (3), i.e., the high frequency limit of permittivity \( \varepsilon_0 \), the dielectric strength \( \Delta \varepsilon_{\text{low}}, \Delta \varepsilon_{\text{high}} \) and the relaxation time \( \tau_{\text{low}}, \tau_{\text{high}} \) of the two modes, can be obtained. The best-fit dielectric parameters obtained are listed in Table 1.

Figure 3-A shows the water content dependence of relaxation strength \( \Delta \varepsilon \) for jujube honey in radio frequency. As can be seen from this figure, the low-frequency relaxation strength \( \Delta \varepsilon_{\text{low}} \) decreases with water and then increases at the water content of 500 mg g\(^{-1}\) (black dash dot line); while the high-frequency relaxation strength \( \Delta \varepsilon_{\text{high}} \) decreases with the water in the whole range. As the amount of water increases, as shown in Figure 3 (B-C), the interface between honey and water will invert: from water/honey (water bubbles in honey, Figure 3-B) to honey/water (honey bubbles in water, Figure 3-C). The inversion of \( \Delta \varepsilon_{\text{low}} \) at 500 mg g\(^{-1}\) is just because of the inverted interface: when the water content is less than 500 mg g\(^{-1}\), the low-frequency relaxation is caused by the interface polarization between water bubbles and honey. The water bubbles in honey will become larger with the increasing water content and honey that contacts with water on per unit surface area reduces, so, the interfacial polarization becomes weakened and \( \Delta \varepsilon_{\text{low}} \) decreases; when the water content is larger than 500 mg g\(^{-1}\), the low-frequency relaxation is caused by the interfacial polarization between honey bubbles and water. The number of water molecules contacting with honey bubbles per unit surface area increases with water, so, the interfacial polarization is enhanced and \( \Delta \varepsilon_{\text{low}} \) increases. Furthermore, the low-frequency relaxation time \( \tau_{\text{low}} \) in Table 1, which is suddenly reduced at the water content of 500 mg g\(^{-1}\) and divides the water content into two regions, also supports the above results.

The high-frequency relaxation in radio frequency is caused by the motions of polar groups in polysaccharide or other macromolecules in honey (Kaminski et al. 2012). With the increasing water content, because of the decrease of dipole per unit volume, \( \Delta \varepsilon_{\text{high}} \) decreases and eventually tends to zero. These results indicate that the

**Table 1.** The dielectric parameters of jujube honey at radio frequency.

<table>
<thead>
<tr>
<th>( w_{\text{water}} ) (mg g(^{-1}))</th>
<th>( \tau_{\text{low}} ) (μs)</th>
<th>( \tau_{\text{high}} ) (μs)</th>
<th>( \Delta \varepsilon_{\text{low}} )</th>
<th>( \Delta \varepsilon_{\text{high}} )</th>
<th>( \varepsilon_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>4.86</td>
<td>0.13</td>
<td>2.60</td>
<td>4.27</td>
<td>45.65</td>
</tr>
<tr>
<td>200</td>
<td>3.69</td>
<td>0.10</td>
<td>1.38</td>
<td>3.54</td>
<td>48.51</td>
</tr>
<tr>
<td>350</td>
<td>4.23</td>
<td>0.46</td>
<td>0.50</td>
<td>1.10</td>
<td>56.51</td>
</tr>
<tr>
<td>500</td>
<td>0.46</td>
<td>0.13</td>
<td>0.32</td>
<td>0.24</td>
<td>61.34</td>
</tr>
<tr>
<td>700</td>
<td>0.61</td>
<td>0.12</td>
<td>0.65</td>
<td>0.16</td>
<td>64.91</td>
</tr>
<tr>
<td>900</td>
<td>0.61</td>
<td>0.13</td>
<td>0.82</td>
<td>0.06</td>
<td>71.90</td>
</tr>
</tbody>
</table>

**Figure 3.** (A) The strength of dielectric relaxation \( \Delta \varepsilon \) of jujube honey at different water contents in radio frequency; the relaxation mechanisms of honey solutions at the water content of < 500 mg g\(^{-1}\) (B), and > 500 mg g\(^{-1}\) (C).
water content significantly affects the dielectric properties of honey, because of the changes in the interfacial property of honey/water and the changes in dipole moment of the macromolecules in honey.

**Dielectric Analysis at 10 MHz to 40 GHz**

As can be seen in Figure 1 (C-D), an obvious relaxation contributed from water molecules is observed in the microwave region. With the increase in water, the relaxation strength is increased and the relaxation gradually moves to higher frequencies. This relaxation actually originates from two contributions, i.e., bound water that interacts with the carbohydrates, protein and fat in honey, and free water that is away from these biological molecules (Fukuzaki, *et al.* 1995, and Mashimo, *et al.* 1987). We can separate the two contributions by fitting the dielectric loss spectra using the software Agilent Vee Pro 7.0.

Figure 4 shows the dielectric loss spectra in microwave for jujube honey solutions at water content of 350, 500, and 700 mg g⁻¹. The hollow symbols represent the raw data and the solid lines are the fitted curves to the raw data. The dash dotted lines are the contribution from free water and the dotted lines are the contribution from bound water. As water increases, the relaxation of bound water moves to higher frequencies and the relaxation strength increases, indicating that more and more water molecules will interact with the nutrient substance in honey, and due to the decreased viscosity, the movement of bound water becomes freer. These results reveal that the water molecules significantly affect the dielectric properties of honey in microwave frequency by interacting with nutrients in honey.

**Difference in the Dielectric Properties of Different Pure Honeys**

The permittivity (A) and dielectric loss (B) spectra for three different pure honeys in microwave frequency are shown in Figure 5. It is clear that the relaxation caused by dipole orientation of water molecules is observed at around 1-2 GHz. The water in pure honey is mainly in bound form, so, this relaxation is mainly caused by bound water. Figure 5-A shows that the permittivity of the honey follows the relation: $\varepsilon_{\text{yellow-locust}} > \varepsilon_{\text{jujube honey}} \approx \varepsilon_{\text{vitex honey}}$, i.e., the yellow-locust honey that contains the maximum water content has the highest permittivity, and the jujube and vitex honey which contain the same amount of water have similar permittivity. This result is
consistent with the water content of pure honey, indicating that different pure honeys with different water contents may be roughly distinguished by dielectric spectroscopy. In addition, the relaxation frequency (blue arrows in Figure 5-B) of the honey follows the relation: $f_{\text{yellow-locust}} > f_{\text{jujube}} > f_{\text{vitex}}$, suggesting that the movement of bound water in yellow-locust honey is freer. Because the composition of honey is relatively complex, and the dielectric properties can be influenced by many factors, such as ash contents (Ahmed et al. 2007, and Galema, 1997), it is difficult to obtain the essential reason for the different dielectric behavior of different types of honey.

CONCLUSIONS

The dielectric behaviors of jujube, yellow-locust and vitex honey solutions were studied at the frequency range from 40 Hz to 40 GHz as a function of water content. Two relaxations, which were caused by interfacial polarization and dipole polarization of macromolecules in honey, respectively, were observed in radio frequency. As the water increases, the inversion of the interface between water and honey can be captured by dielectric spectroscopy. In addition, the permittivity and water content of the honey solutions showed linear relationship, indicating that dielectric spectroscopy is a potential tool to determine the adulterated honey with water. Another relaxation caused by the orientation of water molecules was observed in the microwave frequency. As water increases, the relaxation strength increased and the relaxation gradually moves to higher frequencies, approaching to that of pure water. Meanwhile, it was found that the number of bound water molecules that interact with the nutrients in honey was also increased with water. Besides, the dielectric properties of pure honey were also compared and the results indicated that different pure honeys with different water contents can be roughly identified by dielectric spectroscopy.

This study reveals that the water molecules affect the dielectric properties of honey by changing the interfacial property between honey and water and interacting with the nutrients in honey. It is feasible to detect the honey adulterated with water by dielectric spectroscopy.

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تأثیر آب موجود در عمل روی خواص دی الکتریک پهنای باند آن عسل

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چکیده

در این پژوهش، تأثیر آب موجود در عمل روی خواص دی الکتریک پهنای باند عمل عضای عسل گل درخت (yellow-locust) و عسل ویتکس (vex) در پهنای باند (40 Hz-40 GHz) برسی شد. در بسیاری از این خواص (فرکانس های پایین)، دو ریلکسیشن (relaxation) مشاهده شد که با فضای فیزیکی قطر (dipole orientation) و فصل شرکت (interface polarization) صورت می‌گیرد. در بخش‌هایی مثل آب محدود (bound water) و ریلکسیشن های دیگر هم ناشی از آب آزاد و ملکول‌های ماکرو در عمل عضای عسل گرنتی شد. تحلیل ریلکسیشن‌های جلویی آب در عمل تولید کننده مسئول تغییرات خواص دی الکتریک محلول‌های عسل می‌باشد. انرژی بر این، رابطه‌ای خطی بین گذاردهای (permittivity) در حدود 2/45 GHz و آب موجود در محلول‌های عمل درست شد و جنین اشاره داشت که با روش طیف‌سنجی دی الکتریک، آب موجود در عمل را می‌توان اندازه‌گیری کرد. علاوه بر این، خواص دی الکتریک انواع عسل های خالص را مقایسه کردیم و چنین بیشترین که گذاردهای عمل گل درخت yellow-locust می‌باشد. آب را دارد، از همه بیشتر بوده‌ای بر این قرار باشد. طیف‌سنجی دی الکتریک محلول‌های عسل عسل گوناگون‌ها می‌تواند مقدار مختلفی آب دارد به طور تقریبی از هم کم‌سازی کرده‌ایست. این مطالعه نشان می‌دهد که آب موجود در عمل خواص دی الکتریک آن را تحت تأثیر قرار می‌دهد و اینکه طیف‌سنجی دی الکتریک روی اجرا و گذاشته‌ای تشخیص افزودن تقیی آب به عمل است.