Dielectric study of binary mixtures of edible unsaturated oils

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The dielectric and relaxation parameters of a binary system of edible oils, containing unsaturated fats namely mustard oil and coconut oil/ground nut oil/linseed oil in different proportions by volume are measured at different frequencies and a constant temperature (40°C). It is realized that at the given temperature, the dielectric constant of prepared samples at microwave frequency increases with increasing percentage of impurities. The dielectric loss at microwave frequency also increases with the increase in the amount of added impurity. However dielectric constant at optical frequency tends to decrease under similar conditions. The proposed technique to check the purity of samples at microwave frequencies is found better than the traditionally applied optical technique because here different dielectric parameters like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric relaxation in prepared samples may be determined at a time.

Keywords: Unsaturated oils, Dielectric parameters, Relaxation time
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1 Introduction

Food is fuel for body and keeps our mind fit and working. Spurious and adulterated food products cause abundant loss both physically and mentally. With sophistications in the method of adulteration, it becomes imperative that food we consume must be pure. The use of rapeseed mustard oil is the major cooking oil in India and it is highly recommended in food because it contains two essential fatty acids namely linoleic acid and $\alpha$-linolenic acid which our body cannot make itself. During survey in market it was noticed that edible fats generally available in open market including rapeseed mustard oil (Brassica) are not pure in nature. In recent years, it was noticed that even this oil contains adulterants of different kinds like argemone-mexicana oils which has killer ability as reported by Bansal et al. The percentage of impurities present in edible product varies significantly and agencies like AGMARK and ISI have their own standards for checking their purity. In the present paper, a microwave technique to estimate the purity of edible unsaturated fats is discussed. By using obtained data, different scales are prepared to find the amount of impurities in unsaturated oils, which provide the information whether available product in market is suitable for consumption or should be rejected.

Vegetable oils are triesters formed from glycerol and long chain carboxylic acids often called fatty acids and are commonly referred to as triglycerides. The nature of oils depends on its constituent fatty acids. Most of the natural oils are mixed triglycerides having two or three different fatty acids as shown in Fig. 1. Fatty acids, which make triesters, have long chain of carbon atoms. If in a fatty acid, some of the hydrogen atoms are absent and the usual single bond between the carbon atoms has been replaced by a double bond, then it is unsaturated. Unsaturated oils are liquid at room temperature and they are usually of plant origin like mustard oil, olive oil, canola oil, peanut oil etc. The composition (%) of unsaturated oils considered in this paper is given in Table 1.

It was reported by AGMARK that in several parts in our country, commercially available rapeseed mustard oil (Brassica) has groundnut oil, linseed oil or coconut oil as adulterants. The density of these oils are more or less identical and their presence cannot be easily identified by simple visual inspection. For checking impurities in such samples, traditionally chemical testing of samples and measurement of
refractive index by using Abbe’s Refractometer are applied. In the present communication, microwave technique is used and dielectric parameters of different oils samples are obtained at a fixed temperature 40°C. The obtained results at microwave frequency (9.42 GHz) are compared with those obtained at optical frequency (5.46×10¹⁵ Hz) and static frequency (300 Hz). The dielectric properties of unsaturated oil samples describe their molecular interaction with electromagnetic energy and dependence on the frequency of electromagnetic field as well as on the bulk and microscopic properties of the materials and their composition. In addition to dielectric parameters and relaxation times of these samples, saponification value, iodine value, refractive index and density of prepared samples are also measured.

2 Experimental Details

Samples of mustard oil were collected from the market and chemical testing of these samples was carried out under the guidance of AGMARK, Jaipur to find acceptable samples for consumption i.e. purest samples among the available samples. Groundnut oil, linseed oil and coconut oil were added in mustard oil in different proportions by volume as impurities. By applying the method applied by Jangid et al.⁵ for estimation and measurement of dielectric properties of liquid mixtures at MW frequencies, the dielectric constant and dielectric loss of pure mustard oil and oil containing impurities in different percentages by volume are determined. Various oil samples containing impurities in different proportions were placed in the wave-guide. Microwave power is obtained from X band microwave source and is allowed to propagate through sample, which forms standing waves in guide section after being reflected from the short-circuiting wave-guide. The main quantities to be measured experimentally are \( \alpha_d \) and \( \lambda_d \) for the samples. The standing wave pattern is used to find \( \lambda_d \) and \( \alpha_d \).

The precision of measurement for the wavelength with the available microwave test bench is ± 0.001 cm. Corresponding to this accuracy value, the error in the measurement of \( \varepsilon' \) is estimated. For simplification, involved errors due to non-zero impedance of the short circuit plunger are ignored. The errors of measurement are calculated by using the conventional method of error analysis⁴. This method is valid even if the precision of respective measurements differs. With this method, the accuracy of the measurement for \( \varepsilon' \) is found to be ± 1% while for \( \varepsilon'' \) it is ± 5%.

The dielectric constant \( \varepsilon_\infty = n_D^2 \) at optical high frequency (5.46×10¹⁵ Hz) is determined by squaring the refractive index \( n_D \) for the samples, obtained experimentally by using Abbe’s Refractometer. The measurement of dielectric constant at static frequency 300MHz is done by applying Toshniwal RL-09 dipole meter, which is based on heterodyne beat method.

The saponification value is an index of mean molecular weight of the fatty acids of glycerides comprising oil. Higher the saponification value of oil, larger the percentage of low molecular weight of fatty acids it contains. The saponification value is the number of miligrams of potassium hydroxide required to saponify 1 gm of oil/fat. Refluxing with a known excess of standard ethanolic KOH solution saponifies the oil sample. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid.

The saponification value is calculated by using the relation

\[
SV = \frac{(56.1(B - S) \times N)}{W} \quad \ldots(5)
\]

where, B is the volume in ml of standard hydrochloric acid required for the blank; S, the volume in ml of standard hydrochloric acid required for the sample; N,
the Normality of the standard hydrochloric acid and \( W \) is the weight in gm of the oil taken for test.

The iodine value is a measure of the amount of unsaturation (number of double bonds) in a fat. The iodine value of oil is the number of grams of iodine absorbed by 100 g of oil when determined by using Wij’s solution. The excess of iodine monochloride was treated with potassium iodide and the liberated iodine was estimated by titration with sodium thiosulphate solution.

The following relation is used to calculate the iodine values of samples:

\[
IV = 12.69(B - S)N/W 
\]

where, \( B \) is the volume in ml of standard sodium thiosulphate required for the blank; \( S \), the volume in ml of standard sodium thiosulphate solution required for the sample; \( N \), normality of the standard sodium thiosulphate solution; \( W \), weight in gm of the sample.

The standard values of different parameters for rapeseed mustard oil are listed in Table 2.

### 3 Results and Discussion

The chemical testing of prepared samples was carried out under the guidance of AGMARK, Jaipur. The saponification value (SV), iodine values (IV), refractive indices and densities of prepared samples when coconut oil, groundnut oil and linseed oil are mixed in different proportions by volume as impurity in pure mustard oil are shown in Table 3. It may be noticed that the saponification values of all these oils are higher than that of mustard oil. It is also observed that on mixing impurity in pure mustard oils, initially the SV of mustard oils decreases, but when high percentage of impurity is added then SV starts increasing. The lower value of saponification indicates the larger molecular weight of fatty acids while higher value of SV indicates the presence of other oils. Oils with higher values of saponification are not good for health. The iodine values when coconut oil, groundnut oil and linseed oil are mixed in different proportions as impurity in pure mustard oil are also obtained. The iodine value of coconut oil is much smaller than that of mustard oil but for other two oils, it is comparable to that of mustard oil. It is seen that on mixing impurity in pure mustard oil, initially the IV of mustard oil increases, but when high percentage of impurity is added, then IV starts decreasing. The higher IV indicates that the amount of unsaturation (number of double bonds) is higher. It is also observed that the density of pure mustard oil is marginally higher than other oils. Thus it can be inferred that as the impurity in mustard oil increases, the density of mixture decreases.

The dielectric constant and dielectric loss at microwave frequency of pure mustard oil and oil containing impurities in different percentages by volume are determined by applying following relations:

\[
\varepsilon' = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left[ 1 - \left( \frac{\alpha_d}{\beta_d} \right)^2 \right] 
\]

\[
\varepsilon'' = 2 \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left( \frac{\alpha_d}{\beta_d} \right) 
\]

Here, \( \lambda_0, \lambda_c \) and \( \lambda_d \) are the free space wavelength, cut-off wavelength and wavelength in the dielectric.

### Table 2—Standard values of various parameters for rapeseed mustard oil

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameters</th>
<th>Standard values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Refractive index at 40°C</td>
<td>1.4646-1.4662</td>
</tr>
<tr>
<td>2</td>
<td>Saponification value</td>
<td>168-177</td>
</tr>
<tr>
<td>3</td>
<td>Iodine value</td>
<td>96 to 12</td>
</tr>
<tr>
<td>4</td>
<td>Acid value</td>
<td>Not more than 6.0</td>
</tr>
</tbody>
</table>

### Table 3—Chemical characteristics of applied edible oils

<table>
<thead>
<tr>
<th>Percent impurity</th>
<th>Saponification value (SV)</th>
<th>Iodine value (IV)</th>
<th>Refractive Index</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>185.5</td>
<td>185.5</td>
<td>185.5</td>
<td>98.12</td>
</tr>
<tr>
<td>25</td>
<td>149.1</td>
<td>157.35</td>
<td>135.53</td>
<td>107.23</td>
</tr>
<tr>
<td>50</td>
<td>192.3</td>
<td>161.13</td>
<td>156.81</td>
<td>63.4</td>
</tr>
<tr>
<td>75</td>
<td>221.42</td>
<td>172.32</td>
<td>172.42</td>
<td>47.32</td>
</tr>
<tr>
<td>100</td>
<td>241.13</td>
<td>190.13</td>
<td>188</td>
<td>15.5</td>
</tr>
</tbody>
</table>


\( \alpha_d \) and \( \beta_d \) are attenuation constant of the material measured in nepers per meter and phase shift per unit length of the sample measured in radians per meter, respectively, and are calculated by following relations:

\[
\alpha_d = \frac{2.302}{2L} \log \left[ \frac{x_1}{\sqrt{x_2} - \sqrt{x_1}} \right] \\
\beta_d = \frac{2\pi}{\lambda_d}
\]

\( x_1 \) and \( x_2 \) are output power readings without and with sample of thickness \( L \) in the wave-guide. The experimental values of dielectric constant (\( \varepsilon' \)) and dielectric loss (\( \varepsilon'' \)) at microwave frequency 9.42 GHz are measured and are compared with \( \varepsilon_s \) values obtained at static frequency 300 Hz and \( \varepsilon_\infty \) values obtained at optical frequency (5.46×10^{15} \text{ Hz}), respectively, and are given in Table 4. It is found that dielectric constant (\( \varepsilon' \)) for the samples at microwave frequency varies from 2.16 (for pure mustard oil) to 3.80 (for pure coconut oil), 2.60 (for pure groundnut oil) and 3.07 (for pure linseed oil). These variations are shown in Fig. 2. The dielectric constant of mustard oil is less than those of other three oils considered in this paper. It is observed that at the given temperature, the dielectric constant of all prepared samples increases with increasing percentage of impurities.

The variation of dielectric loss at microwave frequency with added impurity is shown in Fig. 3 which indicates that the dielectric loss at given temperature increases with the increase of heavier component in the mixture (added impurity). This result is on expected lines because the overall rotation of the dipole bearing group, i.e. the carboxyl group \(-\text{COOH}\) becomes more difficult with the increase of the heavier molecules, which results in higher value of dielectric loss. The losses involved with mustard oil in the presence of groundnut oil are more than that in the presence of coconut oil or linseed oil.

The experimental value of dielectric constant measured at static frequency 300 KHz for the samples varies from 3.33 (for pure mustard oil) to 3.90 (for pure coconut oil), 3.62 (for pure groundnut oil) and 3.87 (for pure linseed oil). The experimental values of dielectric constant for the samples measured at optical frequency vary from 2.28 (for pure mustard oil) to 2.07 (for pure coconut oil), 2.14 (for pure groundnut oil) and 2.19 (for pure linseed oil).

| Percentage impurity | \( \varepsilon' \) Mustard + Coconut | \( \varepsilon'' \) Mustard + Coconut | \( \varepsilon' \) Mustard + Groundnut | \( \varepsilon'' \) Mustard + Groundnut | \( \varepsilon' \) Mustard + Linseed | \( \varepsilon'' \) Mustard + Linseed | \( \varepsilon_s \) Mustard + Coconut | \( \varepsilon_\infty \) Mustard + Coconut | \( \varepsilon_s \) Mustard + Groundnut | \( \varepsilon_\infty \) Mustard + Groundnut | \( \varepsilon_s \) Mustard + Linseed | \( \varepsilon_\infty \) Mustard + Linseed |
|---------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 0                   | 2.10                          | 2.10                          | 2.10                          | 2.10                          | 3.33                          | 3.33                          | 3.33                          | 2.28                          | 2.28                          | 2.28                          | 2.28                          | 2.28                          | 2.28                          |
| 25                  | 2.75                          | 2.22                          | 2.45                          | 0.11                          | 3.62                          | 3.35                          | 3.40                          | 2.02                          | 2.22                          | 2.24                          | 2.20                          | 2.22                          | 2.24                          |
| 50                  | 3.05                          | 2.31                          | 2.80                          | 0.21                          | 3.74                          | 3.45                          | 3.61                          | 1.96                          | 2.19                          | 2.22                          | 2.16                          | 2.19                          | 2.22                          |
| 75                  | 3.25                          | 2.45                          | 2.91                          | 0.35                          | 3.82                          | 3.52                          | 3.72                          | 1.83                          | 2.16                          | 2.19                          | 2.13                          | 2.16                          | 2.19                          |
| 100                 | 3.8                           | 2.60                          | 3.07                          | 0.46                          | 3.90                          | 3.62                          | 3.87                          | 2.07                          | 2.14                          | 2.17                          | 2.07                          | 2.14                          | 2.17                          |
oil) and 2.17 (for pure linseed oil). These variations are shown in Figs 4 and 5, respectively. It is found that the dielectric constant at optical frequency \((5.46\times10^{15}\text{ Hz})\) tends to decrease with increase in percentage impurity. The possible reason behind this variation may be that the refractive index tends to increase with the number of double bonds i.e. with mean saturation and iodine value. This behaviour of dielectric constant at optical frequency is opposite to that observed at microwave and static frequencies.

Various dielectric relaxation times are calculated by using the following relations

\[
\tau_0 = \frac{1}{\omega} \sqrt{\frac{\varepsilon_0 - \varepsilon'}{\varepsilon' - \varepsilon_\infty}} \quad \text{...(4a)}
\]

\[
\tau_1 = \frac{1}{\omega} \left( \frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty} \right) \quad \text{...(4b)}
\]

\[
\tau_2 = \frac{1}{\omega} \left( \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon''} \right) \quad \text{...(4c)}
\]

Here, \(\tau_o\) is the most probable time, \(\tau_1\) is the relaxation time due to intermolecular rotation and \(\tau_2\) is the relaxation time due to intramolecular rotation.

The values of most probable relaxation time \(\tau_0\), relaxation time for inter-molecular rotation \(\tau_1\) and relaxation time for intra molecular rotation \(\tau_2\) are calculated following Eqs (4a-4c) and are listed in Table 5. The values \(\tau_0\) and \(\tau_2\) decreases with increase in impurity, while \(\tau_1\) increases with increase in impurity. The \(\tau_2\) values are appreciably higher than \(\tau_0\) and \(\tau_1\) values which indicates that contribution of intramolecular relaxation is higher in comparison to intermolecular or overall molecular relaxation. The \(\tau_0\) values show a systematical variation with concentration ratio of the mixtures at a given temperature. It can be seen that \(\tau_0\) values for both these systems always lie between \(\tau_0\) values of the constituent components at fixed temperature. Such behaviour may be attributed to simple overlap of two individual Debye regions. The \(\tau_0\) values also show that for a composition having nearly 50 percent of each component, these values are equivalent to the mean value of the \(\tau_0\) values of the pure component. This indicates that the degree of overlap of two Debye regions at a particular temperature is nearly same. The

<table>
<thead>
<tr>
<th>Percentage impurity</th>
<th>(\tau_0\times10^{11}) (s.)</th>
<th>(\tau_1\times10^{12}) (s.)</th>
<th>(\tau_2\times10^{10}) (s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mustard + Coconut</td>
<td>1.78</td>
<td>0.82</td>
<td>8.82</td>
</tr>
<tr>
<td>Mustard + Groundnut</td>
<td>1.65</td>
<td>1.31</td>
<td>1.34</td>
</tr>
<tr>
<td>Mustard + Linseed</td>
<td>1.51</td>
<td>3.42</td>
<td>0.55</td>
</tr>
<tr>
<td>Mustard + Coconut</td>
<td>1.2</td>
<td>4.13</td>
<td>0.33</td>
</tr>
<tr>
<td>Mustard + Groundnut</td>
<td>0.04</td>
<td>5.32</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**Table 5—Dielectric relaxation times at microwave frequency**
variations of $\tau_0$ values with concentration of the mixture composition show that in these mixtures a slight widening of dispersion region takes place resulting into a relaxation of the mixture which is resultant of the individual components.

The proposed technique may be applied to check the purity of any liquid samples like for checking the presence of argemone in mustard oil, fluoride content in water, impurities in cold drinks etc.

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