Correlation of Basic Oil Quality Indices and Electrical Properties of Model Vegetable Oil Systems

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Ⓢ *Supporting Information*

ABSTRACT: Model vegetable oil mixtures with significantly different basic oil quality indices (free fatty acid, iodine, and Totox values) were prepared by adding oleic acids, synthetic saturated triglycerides, or oxidized safflower oil (*Carthamus tinctorius*) to the oleic type of sunflower oil. Dielectric constants, dielectric loss factors, quality factors, and electrical conductivities of model lipids were determined at frequencies from 50 Hz to 2 MHz and at temperatures from 293.15 to 323.15 K. The dependence of these dielectric parameters on basic oil quality indices was investigated. Adding oleic acids to sunflower oil resulted in lower dielectric constants and conductivities and higher quality factors. Reduced iodine values resulted in increased dielectric constants and quality factors and decreased conductivities. Higher Totox values resulted in higher dielectric constants and conductivities at high frequencies and lower quality factors. Dielectric constants decreased linearly with temperature, whereas conductivities followed the Arrhenius law.

KEYWORDS: model lipids, dielectric constant, electrical conductivity, free fatty acid value, iodine value, Totox value

■ INTRODUCTION

Vegetable oils and fats are triesters of glycerol and fatty acids, that is, carboxylic acids with long, straight aliphatic chains with 8−24 units. Vegetable oils are very important in human nutrition, as they are sources of energy, essential fatty acids, and other nonpolar nutrients. They are also used in food preparation, for frying and baking, and in food processing, as flavor enhancers and for their effects on product texture. The variations in the chemical compositions of vegetable oils require a number of analytical methods to be used for oil analysis. Chromatographic methods can be used for qualitative and quantitative determinations of specific compounds.[1,2] Other analytical procedures are used to determine the chemical properties of an oil that are typical for the group of compounds, such as their antioxidant activity,[3,4] oil quality indices (acid or iodine values, etc.), or ash content. These analytical methods are time-consuming and often require the use of solvents and reagents[5,6] that are harmful for the environment. In addition to standard methods, and particularly for determining the quality of frying oils, a series of rapid tests can be used that are based on physical properties, such as the determination of viscosity and dielectric constant,[7] or on spectroscopic data with its variety of possibilities.[8] However, often, the connection between a physical property and certain compounds present in a lipid matrix is not straightforward.

Dielectric spectroscopy has emerged as a simple, rapid, and nondestructive technique that can provide information about the dielectric response of a material in an electric field. The dielectric parameters (e.g., the permittivity or dielectric constant, the dielectric loss factor) depend on the composition of complex mixtures and also of the food itself. In general, the dielectric constant reflects the ability of a material to store electromagnetic energy, and the dielectric loss factor represents its ability to dissipate electromagnetic energy. Among foods, fats represent the most insulating of materials, with the lowest

water content and the lowest dielectric constants.[8,9] The use of dielectric constants for determining the deterioration of frying fats started in 1981;[10] this has a variety of commercial implementations and includes Food Oil Monitor 310, Testo 265, Capsens 5000, and others.[7] In recent years, some studies have used the dielectric constant to determine the type of an edible oil[11,12] its polarizability, and its dipole moment,[12,13] as well as how it might have been adulterated.[14,15]

The dielectric properties of most materials vary considerably with the frequency of the applied electric field. At low frequencies, in a static region where the dipoles have time to follow the variations of the applied field, the (real) permittivity, the dielectric constant, is constant and has its maximum value. As the frequency increases, the polar molecule can follow the changes in the direction of the electric field, although only up to a point. As the frequency continues to increase, the dipole motion can no longer keep up with the changing field. As a result, the dielectric constant drops with increasing frequency. In a complex material, several decreasing steps would be expected in the radiofrequency and microwave bands. In the infrared and optical band, there is atomic and electronic polarization. Finally, the dielectric constant levels out to its so-called optical level, or permittivity, for infinite frequency, and its value can be calculated from the refractive index.[16] The static permittivity of edible oils at room temperature has a value from 3.0 to 3.2[11] and a permittivity for infinite frequency of 2.2.[12] Energy absorption in food in the radiofrequency and microwave bands primarily involves two mechanisms: dipolar relaxation and ionic conduction. Dipolar relaxation is the result of dipoles that rotate, alternate, and collide with neighboring

molecules under the influence of the alternating electric field. Ionic conduction results from the ions present in the material, which migrate in the electric field. Both effects generate heat and disperse energy and, consequently, the (imaginary) permittivity–loss factor is high in the dielectric spectrum. Losses from ionic conduction appear at lower frequencies compared to losses from dipolar mechanisms. The loss factor peak, which accompanies the drop in the (real) permittivity, has a maximum at its relaxation frequency and represents a dipolar mechanism. The relaxation process for different types of vegetable oils appears between 4.0 and 5.2 MHz.[13]

The purpose of the present study was to determine the correlations between the electrical properties and the basic oil quality indices [free fatty acid values (FFAs), iodine values (IVs), and Totox values] of model lipid mixtures that are based on the oleic type of sunflower oil. The FFAs measure the content of carboxylic groups, and the IVs reflect the levels of saturation of the fat. The Totox values reflect the total oxidation, which is a combination of the peroxide values (PVs), which measure the presence of hydroperoxides, and the *p*-anisidine values (AnVs), which measure the content of aldehydes. Model lipid mixtures with significantly different FFAs, IVs, and Totox states were prepared by adding fatty acids, synthetic saturated triglycerides, or oxidized safflower (*Carthamus tinctorius*) oil to the sunflower oil. The dielectric constants, dielectric loss factors, and electrical conductivities of these samples were determined at radiofrequencies from 50 Hz to 2 MHz, by measuring the capacitance and resistance. The effect of temperature on the electrical properties of model lipid mixtures was also investigated in the temperature range from 293.15 to 323.15 K. The results of the present study improve our understanding of the interactions of radiofrequencies with edible oils. These results will be useful for quality evaluations of natural and synthetic triglycerides used for human nutrition or biofuel technologies requiring a rapid and nondestructive method.

■ MATERIALS AND METHODS

Model Lipids. Model lipid mixtures were prepared with significantly different FFA, IV, and Totox values. As a basic lipid, the oleic type of sunflower oil from a Slovenian supermarket was used. Model lipid mixtures with different FFAs were prepared from sunflower oil and vegetable oleic acid (Merck, 1.00471), which is a mixture of fatty acids with a high content of oleic acid (78%) (Table 1). The variations in the IVs were achieved by adding synthetic saturated triglycerides to the sunflower oil (Cognis, Delios V liquid), which contain saturated, short-chain fatty acids and are in a liquid state at room temperature. Model lipid mixtures with different Totox values were prepared from sunflower oil and oxidized safflower oil. Safflower oil (*C. tinctorius*, Sigma, S8281) with a high content of linoleic acid (Table 1) and without oxidation protection agents was oxidized by heating it to 65 °C for 260 h. All of the mixtures were prepared by weighing and mixing the two components in different ratios; the sunflower oil contents in the mixtures were 20, 40, 60, and 80%. For degassing and moisture removal, the samples were kept at 298 K under reduced pressure (~15 kPa) for 30 min, just prior to the measurements.

Oil Quality Indices. The FFAs of the oils were determined using the ISO 660 method,[6] with slight modifications, and are reported as percentages of oleic acid. The IVs were analyzed with iodine monobromide using the IUPAC 2.205 method[5] and are calculated as mass (g) of iodine per 100 g of sample. For determination of the sPVs, the AOAC 965.33 method was used and the PVs are expressed as milliequivalents of active oxygen per kilogram of lipid. The AnVs were analyzed and reported according to the IUPAC 2.504 method.[5]

Table 1. Basic Oil Quality Indices, as Well as the Fatty Acid Compositions, of the Lipids Used for the Analysis Mixtures[a]

	quality indices					fatty acid composition (%)							
lipid	FFA (%)	IV (g I₂/100 g)	PV (mequiv O₂/kg)	AnV	Totox	8:0	10:00	12:00	16:00	18:00	18:01	18:02	18:03
sunflower oil	0.835 ± 0.001	85.4 ± 0.7	2.4 ± 0.2	0.17 ± 0.05	4.91 ± 0.5				3.68 ± 0.01	3.24 ± 0.05	84.6 ± 0.1	8.40 ± 0.07	0.088 ± 0.002
oleic acid	100.5 ± 0.6	91.9 ± 0.4	1.2 ± 0.2	16.3 ± 0.2	18.7 ± 0.6			1.5 ± 0.1	4.76 ± 0.07	1.4 ± 0.1	77.9 ± 0.3	14.4 ± 0.2	0.050 ± 0.004
saturated synthetic triglyceride	0.066 ± 0.001	4.1 ± 0.4	0.4 ± 0.1	0.41 ± 0.09	1.1 ± 0.3	53.7 ± 0.7	45.4 ± 0.7	0.43 ± 0.04	0.183 ± 0.007	0.041 ± 0.008	0.14 ± 0.03	0.13 ± 0.08	
oxidized safflower oil	1.6 ± 0.1	97.4 ± 0.9	512 ± 3	249 ± 4	1273 ± 10				7.107 ± 0.004[b]	2.44 ± 0.03[b]	15.96 ± 0.03[b]	74.26 ± 0.05[b]	0.232 ± 0.007[b]

[a]Data are means ± standard error (n = 3). [b]Composition for native safflower oil. Due to the high degree of oxidation the composition of oxidized safflower oil changed; unsaturation was reduced when oxidation products were formed.

The PVs and AnVs were used to calculate the total oxidation, or Totox, according to[17]

$$\text{Totox} = 2 \times \text{PV} + \text{AnV} \qquad (1)$$

All of the measurements were performed in triplicate. Basic oil quality indices were determined for all of the model lipids (Table 1) and for one mixture with an intermediate composition. For the other lipid mixtures, the indices were calculated by linear interpolation.

The fatty acid compositions for the model lipids (Table 1) were determined using gas chromatography of the fatty acid methyl esters (FAMEs) in accordance with IUPAC 2.301 and 2.302.[5] The FAMEs were quantified on an Agilent 6890N gas chromatograph, with a flame ionization detector and an Agilent 7683 autosampler (Agilent Technologies Inc., Wilmington, DE, USA) on an SPB PUFA; a 30 m × 0.25 mm × 0.2 μm column (Supelco) was used.

Dielectric Properties. The dielectric properties were determined by the capacitive method, using an E4980A precision LCR meter and a 16452 A liquid test fixture (Agilent Technologies). After a short compensation of the liquid dielectric test fixture, the parallel capacitance and resistance were measured without and with the samples, at 50 uniformly distributed frequencies in the range from 50 Hz to 2 MHz. All of the measurements were performed in the temperature range from 293.15 to 323.15 K, with steps of 10.00 K and with precision of 0.05 K. The temperature control was performed using a 7320 high-precision water bath (Fluke) and a 5627A/1502A external thermometer system (Fluke).

The dielectric parameters were calculated from the measures of the capacitance and the equivalent resistance of the lipids

$$\varepsilon' = \frac{C_P}{K_c} \qquad (2)$$

where ε' is the dielectric constant, as the real part of the relative permittivity, C_P is the capacitance of the model lipid corrected for "stray" capacitance, and K_c is the mean cell constant. Following Midmore et al.[18] the cell constant and stray capacitance were determined from measurements made with air and cyclohexane, Sigma-Aldrich 227048,[19] at each temperature. The mean cell constant and stray capacitance were computed by averaging the results determined in the optimal frequency range from 10 to 500 kHz.[20] The dielectric loss factor, ε'', as the imaginary part of the relative permittivity, is given as

$$\varepsilon'' = \frac{1}{\omega R_p K_c} \qquad (3)$$

where R_p is the resistance of the lipid sample, ω is the angular frequency ($\omega = 2\pi f$), and f is the frequency. The quality factor, Q, is defined as the tangent of the impedance phase angle, θ, and it is calculated from the ratio of the dielectric constant and the loss or from the capacitance and the resistance:

$$Q = \tan \theta = \frac{\varepsilon'}{\varepsilon''} = R_p C_P \qquad (4)$$

The resistance data can also be represented as the specific electrical conductivity, σ

$$\sigma = \frac{\varepsilon_0}{R_p K_c} \qquad (5)$$

where ε_0 is the permittivity of a vacuum (8.854×10^{-12} F m^{-1}).

All of the measurements were carried out in triplicate. The reproducibility determined as the relative standard deviation was better for the dielectric constant (0.1%) than for the dielectric loss (1%).

RESULTS AND DISCUSSION

Electrical Properties of the Oleic Type of Sunflower Oil. The dielectric constant of the sunflower oil was independent of the frequency in the frequency range from 50 Hz to 1 MHz; it decreased by <0.2% within the frequency range measured even at 293.15 K, at which the differences were most explicit (Figure 1). A similar trend was described by Lizhi
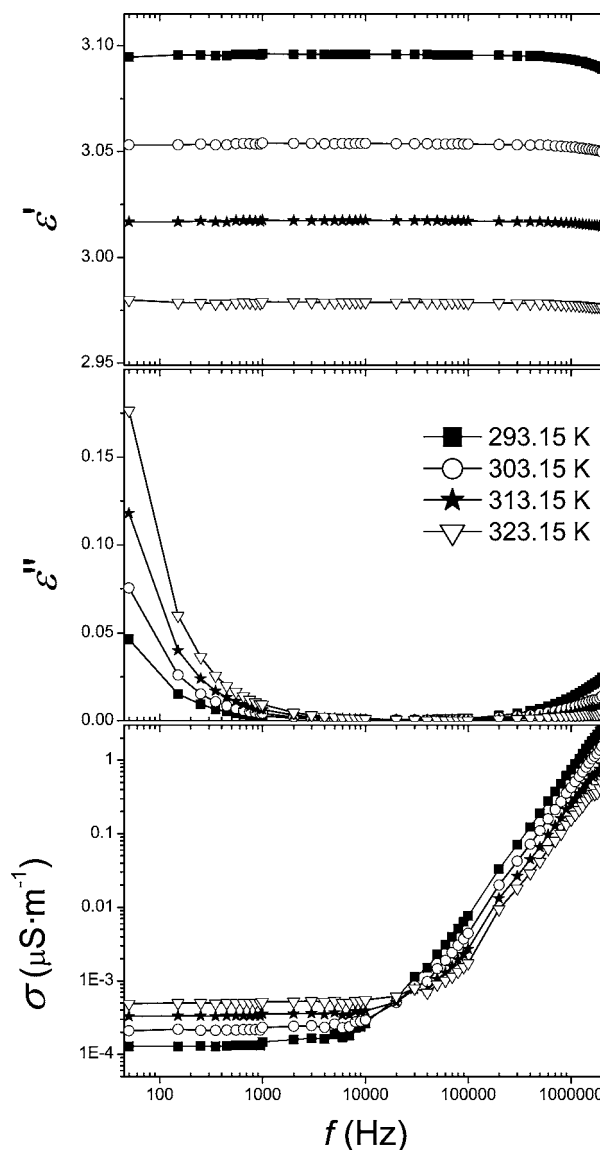

Figure 1. Dependence of the dielectric constant ε', dielectric loss ε'', and conductivity σ (log scale) of the oleic type of sunflower oil on frequency and temperature.

and co-workers.[11] For the vegetable oils, the frequency range used belongs to the static part of the dielectric spectrum. At frequencies >1 MHz, a slight decrease in the dielectric constant was seen, which was most pronounced at 293.15 K. This decrease indicates the beginning of the drop in the dielectric constant with frequency, which is characteristic for the dielectric spectrum in general. The static dielectric constant, ε'_s, which was determined as the average value of the dielectric constants for frequencies from 50 Hz to 100 kHz (Table 2), is comparable with that seen in the literature.[11,12]

The dielectric loss ε'' and the electrical conductivity σ of the sunflower oil were calculated from the resistivity data. The conductivity increased with the frequency, from a few tenths of a nS m^{-1} to μS m^{-1}, and the increase was greater at 293.15 K than at higher temperatures (Figure 1). The dependence of ε'' on the frequency (Figure 1) is similar to that described by Inoue et al.[21] and Lizhi et al.[11] The effects of temperature on ε'' and σ were opposite below and above the minimum (Figure 1). At frequencies <20 kHz the dielectric loss and conductivity increase, whereas at frequencies >60 kHz both parameters

Table 2. Dielectric and Conductivity Data for the Model Lipids at Temperatures from 293.15 to 323.15 K

temp (K)	sample	$\varepsilon'_s{}^a$	$(\varepsilon'/\varepsilon'')_{max} \times 10^{-3\,b}$	$\sigma_0{}^b$ (pS m^{-1})	$\sigma_\infty{}^b$ (μS m^{-1})
293.15	sunflower oil	3.0958 ± 0.0003	13.2 ± 0.4	131 ± 2	22 ± 1
	saturated synthetic triglyceride	3.8520 ± 0.0005	32 ± 2	54 ± 3	10 ± 1
	oxidized safflower oil	3.8535 ± 0.0008	6.1 ± 0.2	66 ± 4	33 ± 1
	sunflower oil and oleic acid (40:60)	2.6814 ± 0.0004	21 ± 2	56 ± 3	6.4 ± 0.6
303.15	sunflower oil	3.0536 ± 0.0002	13.9 ± 0.3	214 ± 3	10 ± 1
	saturated synthetic triglyceride	3.7953 ± 0.0007	34 ± 2	65 ± 3	3.2 ± 0.4
	oxidized safflower oil	3.7925 ± 0.0003	7.5 ± 0.4	106 ± 4	25 ± 1
	sunflower oil and oleic acid (40:60)	2.6488 ± 0.0006	22 ± 1	98 ± 5	2.2 ± 0.3
313.15	sunflower oil	3.0172 ± 0.0002	13.5 ± 0.6	334 ± 2	3.5 ± 0.4
	saturated synthetic triglyceride	3.7418 ± 0.0008	36 ± 2	91.6 ± 0.8	1.0 ± 0.1
	oxidized safflower oil	3.7358 ± 0.0005	8.6 ± 0.4	167 ± 2	17.7 ± 0.9
	sunflower oil and oleic acid (40:60)	2.6253 ± 0.0006	22 ± 1	156 ± 4	0.59 ± 0.07
323.15	sunflower oil	2.9787 ± 0.0003	12.7 ± 0.4	503 ± 1	1.25 ± 0.2
	saturated synthetic triglyceride	3.6824 ± 0.0004	35 ± 2	136.4 ± 0.9	0.2 ± 0.1
	oxidized safflower oil	3.6739 ± 0.0004	6.4 ± 0.4	254 ± 5	10.6 ± 0.6
	sunflower oil and oleic acid (40:60)	2.6001 ± 0.0003	21 ± 1	233 ± 6	0.15 ± 0.03

^{a}Data are means ± standard error for frequencies to 100 kHz (n = 30). ^{b}Uncertainties from fitting procedure.
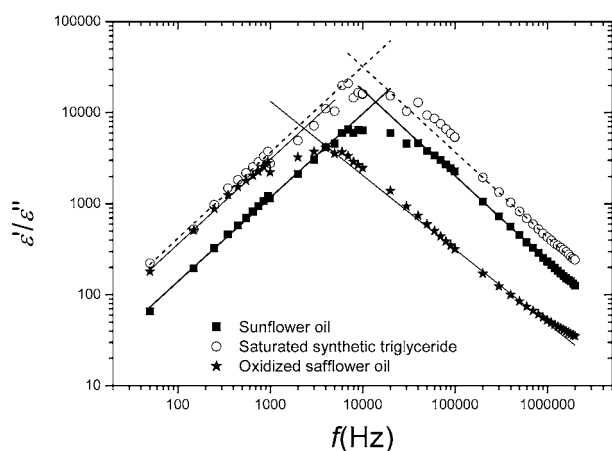

Figure 2. Ratio of dielectric constant and loss ($\varepsilon'/\varepsilon''$) for the sunflower oil, synthetic saturated triglycerides, and oxidized safflower oil at frequencies from 50 Hz to 2 MHz at 293.15 K and the determination of $(\varepsilon'/\varepsilon'')_{max}$.
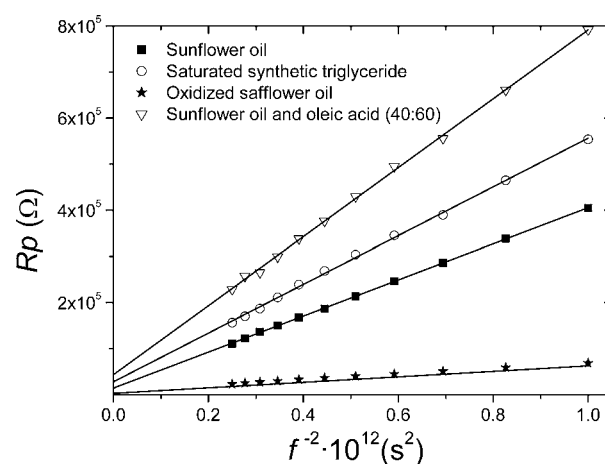

Figure 3. Resistivities of the sunflower oil, synthetic saturated triglycerides, oxidized safflower oil, and the mixture of sunflower oil (40%) with oleic acid (60%) for frequencies from 1 to 2 MHz as a function of the inverse square of the frequency, f^{-2}, and extrapolation to f^{-2} = 0 at 293.15 K.

decrease with increasing temperature. It was previously shown that electrolytic conductivity[22] and loss arising from ionic conduction[9] increase, whereas dipolar loss and its conductive equivalent[9,16] decrease with increasing temperature. For lipids it can be concluded that electrolytic loss and conductivity predominate at frequencies below 20 kHz, whereas the dipolar effect predominates at frequencies from 100 kHz to 2 MHz.

Electrical Properties of the Model Lipids. The trends in the changes of the dielectric constant, the dielectric loss, and the quality factors versus frequency for the model lipids were similar to those of sunflower oil. This is illustrated in the Supporting Information for the saturated synthetic triglycerides, the oxidized safflower oil, the mixture of the sunflower oil and oleic acid (ratio, 40:60), and the sunflower oil, at 293.15 K. The differences in the model lipids can be seen in the static dielectric constant. ε'_s for the saturated synthetic triglycerides and the oxidized safflower oil was higher than that of the sunflower oil, but it was lower for the mixture of the sunflower oil with oleic acid (Table 2). The ε'_s values for oleic acid (78%) of 2.391 at 293.15 K and 2.381 at

303.15 K are comparable with the value of 2.377 determined for oleic acid at 298.15 K by Lizhi and co-workers.[11] The lower dielectric constant for the more polar oleic acid in comparison with the less polar triglycerides was also seen for the carboxylic acids with shorter carbon chains and for their methyl esters,[23] which can be explained by dimerization of the acid molecules over the carboxyl groups in a nonpolar medium.[24]

The differences between the model lipids can also be seen in the dependence of the dielectric loss ε'' and the conductivity σ on frequency. At frequencies below the minimum value of ε'', all of the model lipids had lower ε'' than that for the sunflower oil, with the smallest reduction characteristic for oxidized safflower oil and the highest for saturated synthetic triglycerides (Supporting Information). For mixtures with high contents of oleic acid (>60%), it was not possible to determine ε'', as previously observed for pure oleic acid in studies with similar equipment.[11] When the frequencies increased to 2 MHz, ε''
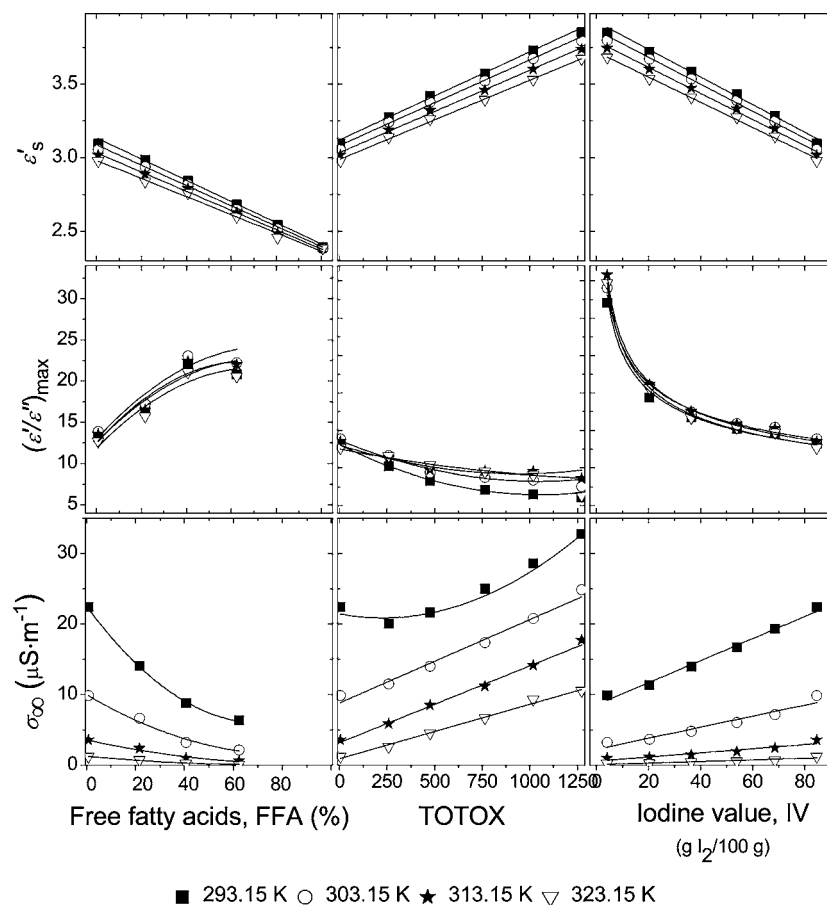
Figure 4. Dependence of the static dielectric constant, ε'_s, the maximum of the ratio of dielectric constant and loss, $(\varepsilon'/\varepsilon'')_{max}$, and the limiting conductivities, σ_∞, of the mixtures of sunflower oil with the model lipids on the FFAs, IVs, and Totox at temperatures from 293.15 to 323.15 K.

■ 293.15 K ○ 303.15 K ★ 313.15 K ▽ 323.15 K

increased the most intensively for the oxidized safflower oil, especially at 323.15 K, and the least for the mixture of oleic acid with the sunflower oil. From the trend for ε' and ε'' at 1−2 MHz, it can be concluded that the drop in the dielectric constant and the peak of dielectric loss, which are characteristic for a dielectric spectrum in general, appear at a lower frequency in oxidized vegetable oil than in the other model lipids. Similar changes for ε' and ε'' with frequency were observed by Inoue et al.[21] for heated soybean oil. The conductivity increased with the frequency, especially for the oxidized safflower oil. For the mixture of oleic acid with sunflower oil and saturated synthetic triglycerides, the conductivity was lower than that for the sunflower oil at all frequencies.

For better representation of the position of the minimum of ε'', the peaks of the ratio of the dielectric constants and loss factors, $\varepsilon'/\varepsilon''$, that is, the quality factors, Q, were determined. These are shown in Figure 2 for the oxidized safflower oil, the sunflower oil, and the saturated synthetic triglycerides. According to eq 4 the quality factor has its maximum at frequencies where ε'' has its minimum. The peak of $\varepsilon'/\varepsilon''$ is lowest for the oxidized safflower oil compared to the sunflower oil and highest for the saturated synthetic triglycerides.

Numerical Evaluation of the Dielectric Spectrum. The dielectric losses of the lipid mixture ε'' were strongly dependent on the frequency; these showed their minima at different frequencies in the range between 10 and 100 kHz, where $\varepsilon'/\varepsilon''$ showed its maxima. The extremes of ε'' and $\varepsilon'/\varepsilon''$ extend over the entire band of frequencies (Figures 1 and 2). The maximum values of $\varepsilon'/\varepsilon''$, as $(\varepsilon'/\varepsilon'')_{max}$ were determined from the linear dependence of $\log(\varepsilon'/\varepsilon'')$ on $\log(f)$ at the frequencies below and above the maximum and as the intersection of both of the straight lines. This procedure is shown in Figure 2. At the lower frequencies (between 50 and 7000 Hz), the straight lines were determined using a correlation coefficient of $r^2 \sim 0.993$ and at higher frequencies (between 0.2 and 1.3 MHz) with $r^2 \sim 0.997$. The data of $(\varepsilon'/\varepsilon'')_{max}$ for the model lipids are collected in Table 2.

The limiting values of electric conductivity were determined from resistivity measurements. The resistivity was independent of the frequency at frequencies below 1 kHz; above 1 kHz, the resistivity decreased distinctly. The limiting values of the conductivity at low frequencies, that is, the direct current or electrolytic conductivity, σ_0, were determined from the average resistivity at frequencies below 1 kHz; the relative standard deviation of determination is $\sim3\%$. The limiting values of conductivity at high frequencies, where conductivity occurred predominantly because of the contribution of a dipolar mechanism to the dielectric loss,[9] σ_∞, were determined from extrapolation of the linear increase in the resistivity with the inverse square of the frequency, f^{-2}, in the range from 1−2 MHz to $f^{-2} = 0$ (Figure 3). The correlation coefficients of the linear regression are $0.990 < r^2 < 0.999$. Both of the limiting parameters for the model lipids are given in Table 2.

The electrolytic conductivities at low frequencies, σ_0, were very low (<0.5 nS m^{-1}), and for the model lipid mixtures they were lower than for the sunflower oil. Higher values of σ_0 were related to the presence of ionic compounds in the samples,[9] which are not an intrinsic property of triglycerides and are not reflected in the selected basic oil quality indices. A higher σ_0 can be compared with the ash content or the charge carrier content in a lipid. Higher σ_0 shows that the edible sunflower oil

contained higher amounts of ionic compounds in some form[25] than the other (synthetic) model lipids.

From Table 2, it can be seen that the model lipids varied in at least one of the parameters observed: lower dielectric constants and limiting conductivities were observed in the case of the mixture of oleic acid and sunflower oil, whereas the saturated synthetic triglycerides showed the highest ε'_s and $(\varepsilon'/\varepsilon'')_{max}$, and for the oxidized safflower oil, higher limiting conductivities at high frequencies, σ_∞ and ε'_s, were characteristic.

Electrical Properties of the Model Lipid Mixtures and the Oil Quality Indices. The values determined for the static dielectric constant, ε'_s, the maximum of the ratio of the dielectric constants and losses, $(\varepsilon''/\varepsilon')_{max}$, and the limiting conductivities, σ_∞, for the mixtures of the model lipids were plotted against the quality index that changed most significantly in comparison to that of the sunflower oil. This is shown in Figure 4, where the symbols indicate the experimental results and the lines correspond to the least-squared fits.

Mixtures containing 0.8−100.5% FFAs (Figure 4) were prepared from the oleic acid and the sunflower oil. The content of the carboxyl group in the mixtures with the highest FFAs was 75-fold higher than in the sunflower oil. In the mixtures with the other model lipids, the variation in FFAs was less significant (<2-fold). The static dielectric constant decreased linearly while the FFAs increased, with this effect being more explicit at lower temperatures. The maximum values of the ratios of the dielectric constants and the losses, $(\varepsilon''/\varepsilon')_{max}$, were higher at higher FFAs and the dependence of $(\varepsilon''/\varepsilon')_{max}$ on the FFAs was a polynomial (second order). Similarly, the decrease in the limiting conductivity σ_∞ was polynomial.

There is no global standard for the determination of the oil quality of frying fats: in Europe, the total polar contents are used,[7] and in Japan and the United States, the acid values are used as the classical methods.[7,21] Inoue and co-workers[21] correlated the increases in the dielectric constants of soybean oil as a result of heating to elevated temperatures with acid value, the analogue of the free fatty acid value. During heating, many chemical processes occur in vegetable oils, not just the hydrolysis of triglycerides, when free fatty acids are also formed. However, a higher content of fatty acids does not result in a higher dielectric constant. Higher dielectric constants in frying fats must be the result of other products that are formed from the hydrolysis, oxidation, and/or polymerization processes.

One of the official methods used for the determination of the deterioration of frying fats is the dielectric constant, which is dependent on the amount of total polar compounds that are formed at elevated temperatures in the fats. The impact of the degree of oxidation on the dielectric spectra was the focus of the present study: safflower oil, which has no preservatives, was stored at 65 °C, to achieve a high degree of oxidation (Table 1) and to avoid other processes that are characteristic of higher temperatures. During the oxidation, the IVs changed from 143 for the native safflower oil to 97.4 for the oxidized safflower oil. The highest Totox value for oxidized safflower oil was 250-fold higher than that in the sunflower oil, whereas the IV was <15% higher and the FFA only 2-fold higher. In the oxidized safflower oil, the contents of the unsaturated fatty acid chains were reduced, especially for C18:3, in comparison with native safflower oil. Higher Totox values resulted in a linear increase in the static dielectric constants at all of the temperatures and a limiting conductivity σ_∞ at temperatures from 303.15 to 323.15 K. The maximum of the ratio of the dielectric constants and the dielectric losses $(\varepsilon'/\varepsilon'')_{max}$ decreased the polynomial (as second

order) with increasing Totox; the effect was less pronounced than for the other quality indices.

According to the literature data, the dielectric constants of vegetable oils are dependent on their saturation[11,12] and consequently on their IVs. Four model mixtures were prepared from the sunflower oil and the liquid synthetic saturated triglycerides, with significantly different IVs and negligibly different FFAs and Totox values (Table 1). Increases in IVs caused linear decreases in the static dielectric constants, a rapid decrease in $(\varepsilon'/\varepsilon'')_{max}$ and a linear increase in the limiting conductivity σ_∞ (Figure 4). The effect of temperature was negligible for $(\varepsilon'/\varepsilon'')_{max}$, in contrast to the dielectric constants and limiting conductivities, for which it was most explicit at 293.15 K.

The saturated synthetic triglycerides were synthesized mainly from caprylic and capric acid, that is, saturated, short-chain fatty acids. In the mixtures of saturated synthetic triglycerides and the sunflower oil, the ester values also varied significantly. Consequently, variations in the dielectric properties can be caused by the lengths of the fatty acid chains or by the ester values. Figure 5 shows the dependence of the dielectric
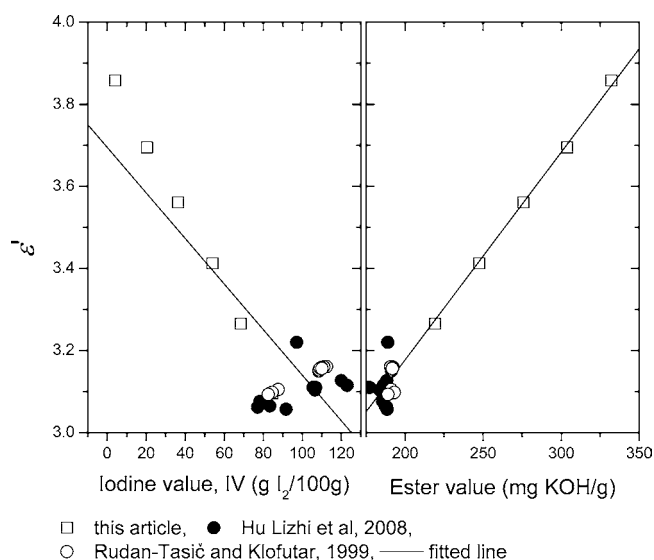

Figure 5. Dependence of the static dielectric constant, ε', on the IVs and ester values.

constants on the IVs and the ester values from both this study and from the literature data.[11,12] For the literature data, where direct measurements of the oil quality indices were not available, the IVs and the ester values were calculated from the fatty acid compositions.[6] The correlation of the overall data for the dielectric constant with the IVs was weaker ($r^2 = 0.702$) than with the ester values ($r^2 = 0.969$). This is important for the analysis of tropical vegetable oils, which contain shorter fatty acid chains (e.g., coconut oil).

Effects of Temperature on the Electrical Properties. The effects of temperature were similar for all of the model lipids; they are presented in Figure 6 for the static dielectric constant ε'_s and the limiting conductivities σ_0 and σ_∞. The symbols indicate the measured values, and the lines represent the corresponding fits.

The dielectric constant, ε'_s, decreased with temperature T, with a good fit to the following linear model:[26]

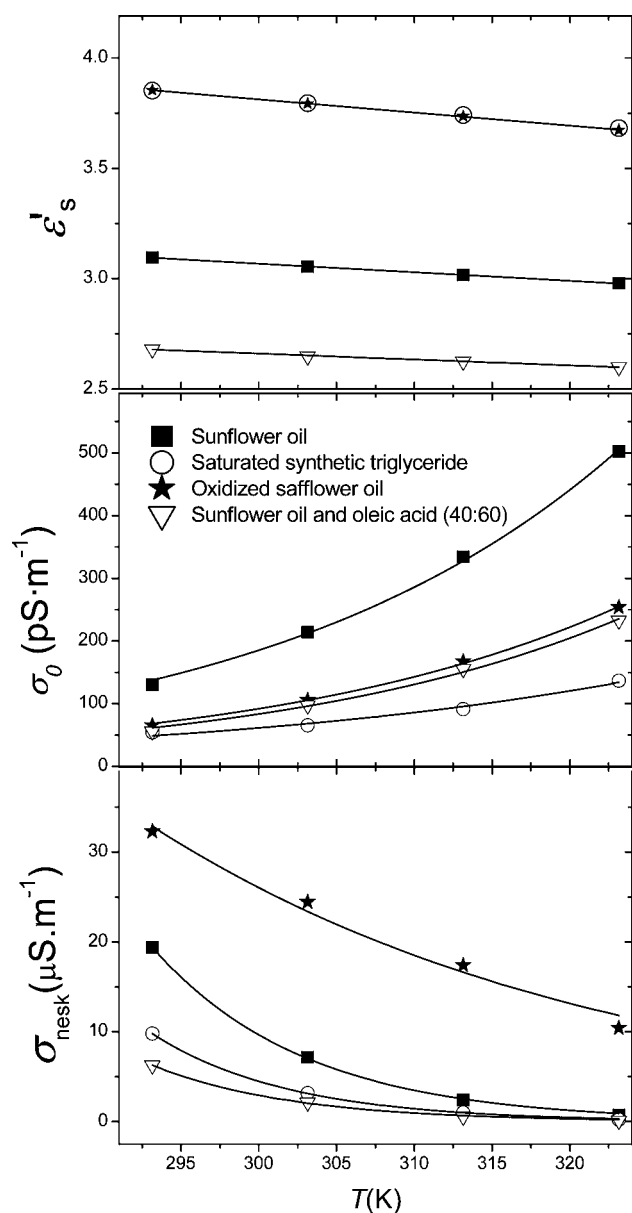$$\varepsilon'_s = \varepsilon'_s(T_0) + \frac{d\varepsilon'_s}{dT}(T - T_0)$$

(6)

Figure 6. Dependence of the static dielectric constant, ε'_s, and the limiting conductivities σ_0 and σ_∞ of the sunflower oil, the saturated triglycerides, the oxidized safflower oil, and the mixture of sunflower oil (40%) with oleic acid (60%) on temperature.

where $\varepsilon_s'(T_0)$ is the fitted value of the static dielectric constant at the reference temperature $T_0 = 298.15$ K. The fitted parameters are given together with their uncertainties in Table 3. For

different types of vegetable oil, Rudan-Tasic and Klofutar[12] found second-order polynomial regression for the dependence of the dielectric constant on temperature, at temperatures from 298 to 313 K. The values of $\varepsilon_s'(T_0)$ and $d\varepsilon_s'/dT$ in this previous study were 3.105 and -0.00832 K^{-1}, respectively (at 298.15 K), for the oleic type of sunflower oil.

The maximum of the ratio of the dielectric constant and the loss $(\varepsilon'/\varepsilon'')_{max}$ was independent of the temperature (Table 2), although the limiting conductivities, σ_0 and σ_∞, fit as a nonlinear curve fit to Arrhenius' law:[26,27]

$$\sigma = A \times \exp(\Delta E_a / RT) \tag{7}$$

A is the scaling coefficient, R is the gas constant (8.31451 J mol^{-1} K^{-1}), and E_a is the activation energy. The Arrhenius dependence and fitted parameters (Table 3) for both of the limiting conductivities, σ_0 and σ_∞, made it possible to relate the conductivities measured at the different temperatures.

The coefficient A_0, as the scaling coefficient for σ_0, was not considered as an intrinsic property of triglycerides,[26] as it depends strongly on the presence of ionic species or contaminants in the lipid. The value of A_0 for synthetic saturated triglycerides is similar to the values of FAMEs produced from different types of vegetable oils.[26] For other model lipids, the value of A_0 (Table 3) was much higher, due to the natural origin and consequently to the possibility that there were various other compounds present in the samples that were charge carriers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
The dependence of dielectric constant, dielectric loss, and conductivity (log scale) of sunflower oil, a mixture sunflower oil and vegetable oleic acid (40:60), saturated synthetic triglycerides, and oxidized safflower oil on the frequency at 293.15 K and the basic oil quality indices of the mixtures of model lipids with the intermediate composition. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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Table 3. Parameters for Dependence of the Static Dielectric Constant, ε'_s, and Limiting Conductivities, σ_0 and σ_∞, on Temperature for Model Lipids

	fitted parameters of the electrical properties								
	ε'_s			σ_0			σ_∞		
sample	$\varepsilon_s'(T_0)$	$-(d\varepsilon_s'/dT) \times 10^3$ (K^{-1})	r^2	A_0 (μS m^{-1})	$(-\Delta E_a)_0$ (kJ mol^{-1})	r^2	A_∞ (S m^{-1})	$(\Delta E_a)_\infty$ (kJ mol^{-1})	r^2
sunflower oil	3.075 ± 0.001	3.88 ± 0.08	0.9991	225	35.0 ± 0.3	0.9997	3.3 × 10^{-17}	66 ± 4	0.9948
saturated synthetic triglyceride	3.824 ± 0.001	5.62 ± 0.08	0.9996	3.0	27 ± 3	0.9661	6.5 × 10^{-21}	85 ± 2	0.9992
oxidized safflower oil	3.823 ± 0.001	5.96 ± 0.07	0.9997	139	35.5 ± 0.2	1.0000	7.1 × 10^{-10}	26 ± 3	0.9663
sunflower oil and oleic acid (40:60)	2.666 ± 0.002	2.68 ± 0.14	0.9945	164	36 ± 1	0.9976	8.2 × 10^{-21}	84 ± 5	0.9971

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