Physical Properties of Triglycerides IV: Dielectric Constant

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Dielectric constants at 20° and at 40° C of a number of triglycerides in the liquid state have been measured. A molar additive function of the dielectric constant, based on a relation derived by J. van Elk, was used in combination with a previously derived equation for triglycerides to give an equation which relates the dielectric constant of a triglyceride or triglyceride mixture to its refractive index, density, and iodine value. Quantification of this relation was based on prime data obtained from these model triglycerides and from previously published data on fatty acid methyl esters.

Physical Eigenschaften von Triglyceriden IV: Dielektrizitätskonstante


Additive Functions of the Dielectric Constant

One of the first attempts to predict the dielectric constant, \( \varepsilon \), from structural contributions was presented by C. B. Thwing*, who proposed the following relation:

\[
\varepsilon = C/C_0
\]

(1)

and the dielectric constant thus defined is dimensionless. This value, also called the static or the quasi-static dielectric constant, is measured in a static field or in an alternating electric field of low frequency.

The first systematic measurements on the dielectric constant of fatty acids and triglycerides were carried out more than half a century ago; L. Kahlenberg¹ observed that the dielectric constant of natural fatty oils with the investigated substance between the plates, \( C \), and the capacitance when a vacuum separates the plates, \( C_0 \). Hence,

\[
\varepsilon = C/C_0
\]

(2)

Introduction

The dielectric constant of a material, \( \varepsilon \), is defined as the ratio of the capacitance of a condenser with the investigated substance between the plates, \( C \), and the capacitance when a vacuum separates the plates, \( C_0 \). Hence,

and the dielectric constant thus defined is dimensionless. This value, also called the static or the quasi-static dielectric constant, is measured in a static field or in an alternating electric field of low frequency.

The first systematic measurements on the dielectric constant of fatty acids and triglycerides were carried out more than half a century ago; L. Kahlenberg¹ observed that the dielectric constant of natural fatty oils with a high percentage of oleic acid was quite similar to the dielectric constant of the acid itself. In the following years only a small number of studies with triglycerides have been reported. A review by W. S. Singleton² adequately covers this subject up to 1958. Of the more recent papers mention can be made of the investigations of K. H. Liitze³ on the dielectric and refractometric behaviour of fats on aging. Of interest is also the correlation between the dielectric constant and the iodine value, which R. R. Allen⁴ observed over the commercially important range of fatty oils.  

Additive Functions of the Dielectric Constant

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\varepsilon = C/C_0
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(2)

Present addresses:

¹ Chevron Research Co., Richmond, Calif., U.S.A. 94802.
² Technische Hogeschool Twente, Enschede, The Netherlands.
⁵ Fette · Seifen · Anstrichmittel 61, 1156 [1959].
⁶ J. Amer. chem. Soc. 82, 671 [1955].
⁷ Z. physik. Chem. 14, 286 [1894].

Propréties physiques des triglycérides IV: Constante diélectrique

La constante diélectrique à 20 ou 40°C a été trouvée sur un nombre de triglycérides à l'état liquide. A l'aide d'une équation précédemment dérivées pour les triglycérides, conjointement avec une fonction additive molaire de la constante diélectrique, qui est basée sur une relation obtenue par J. van Elk, on a établi une relation qui fournit les relations entre la constante diélectrique d'un triglycéride ou d'un mélange de triglycérides et leur indice de réfraction, densité et indice d'indice.

Физические свойства триглицеридов. Сообщение 4: диэлектрическая постоянная.

Для ряда триглицеридов в жидком состоянии определены диэлектрические постоянные. С помощью ранее выведенного уравнения для триглицеридов и молярной аддитивной функции диэлектрической постоянной, байерящейся на полученным вы. Зольком соотношении, получено уравнение для соотношения между диэлектрической постоянной триглицеридов и смеси триглицеридов и их коэффициентом пре- ломления, плотностью и вязким числом. Приводятся количественные данные о соотношении на основании опубликованных данных для метиловых эфиров жир- ных кислот.

In this relation \( z \) stands for the fraction of the atom \( i \), and \( c \) is the number of the atoms \( i \) in the molecule. \( M \) stands for the molecular weight and \( d \) is the density.

Additive behaviour was ascribed to this function and C. B. Thwing obtained excellent results for many compounds. Other investigators have, however, noted significant differences between predicted and observed values. P. Walden⁵ mentions tetramethane for which 104.5 is predicted whereas a value of only 2.1 is observed. To obtain improved predictions P. Walden assumed atomic groups to contribute to the dielectric behaviour. A distinction is made between dielectrophoric and dielectrogenic groups. The high contribution of a dielectrophoric group is only noticeable in the presence of a dielectrogenic group in the same chain.

H. Kaufmann⁷ made a further study on the influence of these groups in different positions in the molecule. He observed the general trend in homologous series, the influence of branching, unsaturation, and substitution on the value of the dielectric constant.

The chief deficiency in all these methods is the inability to account for changes in configuration or for geometrical isomers, and it is in exactly these areas where dipole moment measurements have been very successful in resolving structural problems. The correct additive formula should, therefore, contain vectorial terms to account for those molecular structures, whose contribution to \( \varepsilon \) depends on its direction in space.

Existing additive functions are, however, still quite adequate if one would only restrict the applicability to a limited area. In our particular case, where we have limited ourselves to triglycerides with non-polymerized, non-conjugated, straight-chain component fatty acids, we have noted that good results are obtained by the use of a semi-empirical additive function for homologous series recently derived by J. van Elk⁸. This function reads:

\[
\varepsilon = z \varepsilon_0 + \sum z_i \varepsilon_i
\]

(2)

⁵ Z. physik. Chem. 70, 584 [1910].

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\[ E_m = (\varepsilon - 1)^{1/2} \frac{M}{d} = \sum q_i \]  

In analogy to other molar quantities described in this series of communications we will term \( E_m \) the molar dielectric constant. It has the same dimensions as the molar volume and the molar refraction, i. e., ml/gmole. In our particular case \( E_m \) is not obtained by summation of atomic, but of group contributions. To ensure improved accuracies we will consider the largest groups possible in our area of study without the sacrifice of versatility.

**Experimental**

**Apparatus**

Measurements have been carried out on a commercial Multi-DK-meter (type DK 05-22 manufactured by Dr. Slevogt, Weilheim). A description of the apparatus and the measuring procedure have already been published in the literature.

**Calibration**

The purification of calibration liquids for dielectric measurements has already been discussed in details by E. Oehme and R. R. Mecke and coworkers. Almost all standards used in these investigations have been purified along the discussed lines. The compounds chosen as standards, viz., benzene, cyclohexane, di-n-butyl ether, carbon tetrachloride, 1,2-dichloroethane, and chlorobenzene, were already available in relatively high purity. Depending on the compound the final purification of these products consisted of either a chemical clean-up procedure and/or careful distillations through packed columns. Purity control measurements included determination of the melting point, the UV-spectrum and the use of gas chromatography.

**Drying**

Because of the high dielectric constant of water, absolute dryness of the products under investigation is essential to ensure accurate results. Drying can most conveniently and elegantly be carried out by immersing the products well above their melting points, if necessary. Occasional agitation during at least 10 minutes the first runnings are thrown away and the dried liquid is run into the dry measuring cell.

\[ \Delta E = \frac{E_m}{\varepsilon} - 1 \]

**Temperature**

Readings were taken with calibrated thermometers, the control being better than 0.02° C at 20° C and 0.1° C at 40° C.

**Products**

The investigated products included all mono-acid triglycerides with even-numbered component fatty acids up to trilaurin, a number of mono-acid unsaturated triglycerides, and some mixed triglycerides. Their preparation and physical properties have already been described in previous communications.

**Results**

With a single exception we could not ascertain any comparable data in the literature. The observed dielectric constants at 20° C have been included in Table 1 and those at 40° C in Table 2. \( E_m \) is the molar dielectric constant. The molar volume, \( M/d \), has been obtained from a previous paper and \( \frac{\Sigma E_m}{m} \) is the sum of the molar dielectric constants of the component fatty acid methyl esters. Values of \( E_m \) for the fatty acid methyl esters have already been published previously. The difference between \( E_m \) of the triglyceride and the \( \frac{\Sigma E_m}{m} \) of its component fatty acids in the methyl ester form is called \( \Gamma \), the glyceride increment. \( \Delta \varepsilon \) is the increment of the double bond. It has been obtained as one third the difference between the relative compounds. The \( E_m \) of tristearin, included to facilitate comparison, has been computed by subtracting the average \( \Gamma \) from three times the \( E_m \) of methyl stearate.

**Correlation of Physical Constants**

For a homologous series of organic compounds the additive molar dielectric constant of any member may be expressed by:

\[ E_m = A + n E_{CH_2} \]  

\( A \) is a constant, \( n \) is the term number or the number of C atoms in the chain, and \( E_{CH_2} \) is the \( CH_2 \) increment. This equation has already been quantified earlier for the saturated fatty acid methyl esters. Prime data were obtained on all members of this series from acetate to decanoate.

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Table 2
Dielectric Constant and Derived Values of Triglycerides at 40°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \varepsilon )</th>
<th>( E_m )</th>
<th>( E_F )</th>
<th>( \Sigma E_m )</th>
<th>( \Gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triacetin</td>
<td>6.904</td>
<td>726.3</td>
<td>921.0</td>
<td>194.6</td>
<td></td>
</tr>
<tr>
<td>Tributyrin</td>
<td>5.069</td>
<td>854.5</td>
<td>1066.5</td>
<td>152.0</td>
<td></td>
</tr>
<tr>
<td>Tricaprin</td>
<td>4.280</td>
<td>976.5</td>
<td>1122.2</td>
<td>145.5</td>
<td></td>
</tr>
<tr>
<td>Tricaprylin</td>
<td>3.799</td>
<td>1086.6</td>
<td>1257.2</td>
<td>150.7</td>
<td></td>
</tr>
<tr>
<td>Tricaprin</td>
<td>3.480</td>
<td>1191.4</td>
<td>1346.3</td>
<td>154.9</td>
<td></td>
</tr>
<tr>
<td>Trilaurin</td>
<td>3.281</td>
<td>1305.5</td>
<td>1458.8</td>
<td>153.3</td>
<td></td>
</tr>
<tr>
<td>Tristearin</td>
<td></td>
<td>1634.4</td>
<td>1787.4</td>
<td>153.0</td>
<td></td>
</tr>
<tr>
<td>Triolein</td>
<td>3.028</td>
<td>1673.4</td>
<td>1815.8</td>
<td>142.4</td>
<td></td>
</tr>
<tr>
<td>Trilinolein</td>
<td>3.353</td>
<td>1929.7</td>
<td>2187.8</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td>Trielaidin</td>
<td>2.980</td>
<td>1649.2</td>
<td>1857.8</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td>1-Oleodipalmitin</td>
<td>3.023</td>
<td>1577.4</td>
<td>1724.2</td>
<td>146.8</td>
<td></td>
</tr>
<tr>
<td>2-Oleodipalmitin</td>
<td>3.006</td>
<td>1569.7</td>
<td>1724.2</td>
<td>145.5</td>
<td></td>
</tr>
<tr>
<td>1-Palmito-2-oleostearin</td>
<td>2.975</td>
<td>1606.7</td>
<td>1760.2</td>
<td>156.5</td>
<td></td>
</tr>
<tr>
<td>1-Palmito-2-stearo-olein</td>
<td>2.970</td>
<td>1603.5</td>
<td>1760.2</td>
<td>156.8</td>
<td></td>
</tr>
<tr>
<td>1-Oleo-2-palmitostearin</td>
<td>2.978</td>
<td>1606.9</td>
<td>1760.2</td>
<td>153.4</td>
<td></td>
</tr>
</tbody>
</table>

nonadecanoate. The regression equations for the even members of the series read:

\[ E_m = 276.84 + 18.245 n \]  
\[ 20° C \]  
\[ E_m = 264.53 + 18.355 n \]  
\[ 40° C \]

Due to the phenomenon of alternation, which we observe in the dielectric constant, the even and the uneven members form two series running distinctly parallel to each other. As the relations, which have been developed in these studies, are primarily designed for application in the field of technical lipids, where even-numbered component fatty acids predominate, cognizance of the alternation effect is necessary for improved accuracy.

In a previous communication we have already derived a general equation relating a specific property of an additive function of a triglyceride or triglyceride mixture to \( S. V. \), its saponification value, and to \( I. V. \), its iodine value. For the specific case of the dielectric constant the equation reads:

\[ E_{sp} = E_m / M = 7.13 \cdot 10^{-4} E_{CH_2} + \\ 5.94 (3 A - \Gamma) - 56.78 E_{CH_2} \cdot 10^{-4} S. V. + \\ + (5.66 E_{CH_2} + 39.39 E_F) \cdot 10^{-4} I. V. \]  

\[ (6) \]

\( E_{sp} \) is the specific dielectric constant, which is obtained by dividing \( E_m \) by the average molecular weight \( M \). \( A \) is a constant from equation (5), \( E_{CH_2} \) the CH₂ increment, \( E_F \) the increment of the double bond, and \( \Gamma \) is the glyceride increment.

For the quantification of this relation we have to substitute the prime numbers obtained from our measurements on the model compounds. \( E_{CH_2} \) and \( A \) are already given in equation (5). \( \Gamma \) is obtained as the average differential value of all investigated triglycerides and their corresponding \( \Sigma E_m \). We have deleted the values of triacetin because of the marked effect of the primary terms. Significant deviations are also noted in the polyunsaturated triglycerides. This is due to the deficit to account for configuration effects as already discussed earlier in the section on additivity. These values have, therefore, also been deleted. An average value of 153 for \( \Gamma \) is suggested for both temperatures.

Fig. 1. \( \varepsilon = f (n, d, I. V.) \)

The \( van \ Elk \) relation is probably unsuitable for polyunsaturated compounds. The differential values for \( E_m \) increase sharply with increasing unsaturation in the same chain. For this reason we should, in the case of the dielectric constant, restrict ourselves in our further discussions to saturated and mono-unsaturated fatty acids and their triglycerides. With this restriction \( UF \) would be approximately 13 units at both the investigated temperatures.

Fig. 2. Cross-section of Three-dimensional Diagram for Triglycerides at \( I. V. = 50 \)
Combination of equations (7b) and (8) leads to:

$$\varepsilon = (7.84d - 19.71 \frac{n_D^2 - 1}{n_D^2 + 2} + 8.63 \cdot 10^{-4} I.V. d)^{1/3} + 1 \quad (9)$$

All physical constants in this equation are to be taken as their values at 40° C. A practical solution of this equation is given in the nomograph presented in Fig. 1.

With the aid of this equation we can now also construct planes of constant dielectric constant in a three dimensional diagram with the refractive index, density, and the iodine value on the three mutually perpendicular axes. This diagram has already been mentioned in previous communications15-17, where equations were presented to draw planes of constant molecular weight, dispersion, and ultrasonic sound velocity. Cross-sections of this diagram at I. V. 50 and I. V. 100 are given in Figures 2 and 3.

This diagram is, therefore, suitable for obtaining an insight on the relative dependence of physical properties on each other. For this purpose we have constructed a special cube, a picture of which is given in Plate 1.

Fig. 3. Cross-section of Three-dimensional Diagram for Triglycerides at I. V. = 100

By substituting these prime values in equation (6) we now obtain:

$$20^\circ C \quad E_{sp} = 1.301 + 2.99 \cdot 10^{-3} S. V. + 6.15 \cdot 10^{-4} I.V. \quad (7a)$$

$$40^\circ C \quad E_{sp} = 1.309 + 2.76 \cdot 10^{-3} S. V. + 6.16 \cdot 10^{-4} I.V. \quad (7b)$$

Due to the imposed restrictions these equations are only valid for triglycerides with non-conjugated, non-polymerized, straight-chain component fatty acids with an even number of C-atoms, containing at least 4 C atoms and having not more than one cis- double bond per chain.

Three-dimensional Diagram

The equation relating the specific refraction to the saponification and iodine values has already been derived previously16. At 40° C this relation reads:

$$r_{sp} = \frac{n_H^2 - 1}{n_H^2 + 2}, \quad 1 = 0.33133 - 1.402 \cdot 10^{-4} S. V. \quad (8)$$

$$\pm \quad 1.253 \cdot 10^{-5} I.V.$$