

Physical Properties of Fatty Acid Methyl Esters.

V. Dielectric Constant

T. H. GOUW¹ and J. C. VLUGTER, Department of Chemical Engineering, Technological University, Delft, The Netherlands

Abstract

The dielectric constants of methyl oleate, linoleate, linolenate, erucate and of saturated fatty acid methyl esters acetate through nonadecanoate have been measured at 20 and 40C in the liquid state. The data of the saturated compounds have been correlated with the Smittenberg relation. We computed molar additive properties and increments for the CH₂ group through the Van Elk relation. For the saturated members of the series alternation is observed in the liquid state.

Introduction

THE MAJORITY OF PAPERS on the relation between dielectric behavior and structure concerns itself with the related subjects of dielectric loss and the measurement of the dipole moment. Both these quantities are directly related to the structure of the investigated substance. Questions involving choice of configurations between isomerides, for instance, have often been successfully solved by the measurement of the dipole moments. In this communication, however, we will restrict ourselves to ϵ , the dielectric constant. Reviews on the possible application of ϵ to structural analysis have been presented by Smyth (23) and by Oehme (17,19).

The ϵ of fatty acids and their esters has been the subject of a relatively small number of studies. Reference is made to Singleton's review (21) which covers this subject up to 1958. Of the more recent papers, mention can be made of Lüdde (13) who investigated the dielectric and refractometric behavior on the aging of fats. The relation between ϵ and the I.V. has been studied by Bogdanov and Stepanenko (2) for some triglycerides and some unsaturated C₁₈ fatty acids, and by Allen (1) for the commercially important range of fatty oils. A comparative study of the *cis* and *trans* forms of unsaturated fatty acids has been carried out by Volarovich and Stepanenko (25) and by Phadke (20). The latter author also measured a number of fatty acids and derived relations between ϵ and n (the number of C atoms in the fatty acid chain) and $d\epsilon/dT$ and n . Measurements in the microwave region have been executed by Buchanan (3) on pure fatty acids and their methyl esters.

Experimental

Apparatus. Measurements have been carried out with a commercial unit, the Multi-DK-meter type DK 06-22. This apparatus is manufactured by Dr. Slevogt, Weilheim, Germany. A description of the apparatus and the measuring procedure have already been described elsewhere (19).

A round demountable type measuring cell, which is provided with a thermostating jacket, has been used in our investigations. This cell was developed and built by ourselves and had minor refinements over the commercially available type. All measurements were carried out relative to vacuum, i.e. the capaci-

tance of the cell was always first measured with vacuum (< 1 Torr) between the plates before measurement with the liquid. Measurements were carried out at 500 and 150 kc at 20 and 40C.

Calibration. The preparation of pure liquids for dielectric calibrations has been discussed in detail by Oehme (17,19) and by Mecke et al. (15). The majority of the standards used to calibrate the scale of the precision condenser have been prepared along the discussed lines. Benzene, cyclohexane, di-*n*-butyl ether, carbon tetrachloride, 1,2-dichloroethane and chlorobenzene were chosen as standards. The majority of these products were already available in a relatively pure state. Benzene, cyclohexane and di-*n*-butyl ether were first subjected to a chemical clean-up procedure (15,19). The final purification of all standards was carried out by repeated careful distillations through packed columns with separating capacities ranging from 15-50 theoretical plates. Only the heart-cuts, boiling in a temp range of less than 0.02C, were applied in our investigations. Purity determinations included measurements of the melting point, U.V. and gas chromatography. The values accepted as standards are presented in Table I. Each compound was measured twice at each temp. The regression equation was computed from all the observed data.

Drying. Water has a very high ϵ and 0.01% moisture is sufficient to alter the value of the third decimal place of the dielectric constant. Great care is, therefore, necessary to ensure complete dryness of both the cell and the investigated substances.

Drying of all products was effected by fresh type A4 Linde molecular sieves. Very low residual water contents are claimed by the use of these zeolites (16, 18). Use is made of a chromatographic column with a funnel at the top and a fritted glass filter on the bottom just above a teflon stop-cock. This column is filled with molecular sieves and the liquid is poured into the tube. After occasional agitation during at least 10 min the first runnings are thrown away and the liquid is run into the dry measuring cell.

As far as the viscosity allowed, the higher members were also subjected to the same treatment at more elevated temp. The column was also equipped with a jacket through which hot water could be circulated to keep the product well above the melting point.

Temperature. Temp readings were carried out with calibrated thermometers. Control was better than 0.02C at 20C and better than 0.1C at 40C.

Products. We measured the ϵ of the saturated fatty acid methyl esters acetate through nonadecanoate, methyl oleate, linoleate, linolenate and erucate. Their preparation, purity, density, refractive index, disper-

TABLE I
Dielectric Constant of Calibrating Agents

Product	20C	40C	Ref.
Benzene	2.2835	2.2433	(14,16)
Cyclohexane	2.0228	1.9908	(14,19)
Dibutyl ether	3.0830	2.9412	(16)
Carbon tetrachloride	2.2363	2.1963	(16)
Chlorobenzene	5.708	5.369	(14)
Dichloroethane	10.65	9.54	(14)

¹ Present address: California Research Corp., Richmond, Calif.

TABLE II
The Smittenberg Relation for Saturated Fatty Acid Methyl Esters

$n \geq$	T	ϵ_∞	A	B	σ
2	20C	2.1505	19.1225	1.7421	0.0184
	40C	2.1512	17.2983	1.7417	0.0301
6	20C	2.0927	20.4121	2.0718	0.0109
	40C	2.0997	18.6158	2.1470	0.0102

sion and ultrasonic sound velocity have been reported in previous communications (6,7,8,9).

Results. With the exception of a few older measurements on the lower members of the saturated series, there are no comparative data available in the literature. The available values differ considerably from each other, probably due to the presence of impurities and small amt of water.

Measurements were carried out at a frequency of 500 kc and the obtained values are assumed to be the quasi-static ϵ . Control measurements have also been carried out on the extreme members of the investigated compounds at a frequency of 150 kc. The obtained values corresponded to the first obtained data within the limits of measurement error.

Dielectric constants of the saturated esters are included in Table III and those of the unsaturated members in Table V.

The standard deviation of error in the measurements is estimated at 0.01 units in ϵ . The observed values are, therefore, only accurate to the second decimal place, but an additional decimal is presented for statistical purposes.

The Smittenberg Relation

The Smittenberg (22) relation correlates a physical constant to the chain length of the members of a homologous series. The applicability of this relation to the ϵ of the saturated fatty acid methyl esters has been investigated.

$$\epsilon = \epsilon_\infty + A/(B + n) \quad [1]$$

A and B are constants, n is the term number or the number of C atoms in the fatty acid chain, and ϵ_∞ is the dielectric constant of the limiting fatty acid methyl ester.

We noted that a fair approximation of the ob-

served data was possible by the use of this relation. To obtain the most probable values of A, B and ϵ_∞ , the method of the least squares was applied. The results are presented in Table II.

σ is the standard error of estimate between predicted and measured values. As noted in the other physical properties investigated (6,7,9) the largest deviations occur in the first two members of the series. A significant improvement in fit is obtained by deleting the first four terms and computing the constants only for methyl caproate and the higher homologs. These values are presented in the bottom of Table II. The observed improvement is, however, less marked in comparison to the behavior of those other physical properties.

The value of σ is slightly higher than expected from the level of accuracy of the measurements. A comparison between observed values and those computed from equation 1 using the constants for $n \geq 6$ show that even numbered members are generally lower than the predicted values and alternately the odd members are almost always higher than predicted. We will revert to this phenomenon in the molar dielectric constant.

Additive Functions of the Dielectric Constant

One of the first attempts to predict the ϵ from structural contributions was presented by Thwing (24), who proposed the following relation:

$$\epsilon M/d = \sum_i c_i z_i \quad [2]$$

In this relation z is the increment of the atom i, and c is the number of the atom i in the molecule. Although Thwing obtained excellent results for many compounds, other investigators have, however, noted significant deviations between predicted and observed data. Walden (36) mentions tetranitromethane for which 104.3 is predicted whereas a value of only 2.1 is observed. To obtained improved predictions Walden assumed atomic groups to contribute to ϵ . He distinguishes between dielectrophoric and dielectrogenic groups and noted that the high contribution of a dielectrophoric group is only noticeable in the simul-

TABLE III
Dielectric Constant of Saturated Fatty Acid Methyl Esters

Compound	Measured		Pred eqn. 2; $n \geq 6$		E_m^{20}	$E_{CH_2}^{20}$	E_m^{40}	$E_{C_2H_5}^{40}$
	ϵ^{20}	ϵ^{40}	ϵ^{20}	ϵ^{40}				
Acetate	7.287	6.852	7.106	6.589	315.0		307.0	
Propionate	6.180	5.748	6.117	5.717	330.5	15.5	317.9	10.9
Butyrate	5.432	5.095	5.454	5.128	347.3	16.8	335.5	17.6
Valerate	4.992	4.721	4.979	4.704	368.6	21.2	357.7	22.2
Caproate	4.615	4.368	4.621	4.385	385.9	17.4	374.1	16.3
Oenanthatate	4.355	4.151	4.343	4.135	406.2	20.2	395.8	21.7
Caprylate	4.101	3.930	4.119	3.934	421.7	15.5	412.4	16.7
Pelargonate	3.943	3.779	3.936	3.770	442.7	21.0	432.5	20.0
Caprate	3.785	3.624	3.784	3.632	460.3	17.6	448.8	16.3
Undecanoate	3.671	3.528	3.654	3.516	480.6	20.2	470.0	21.2
Laurate	3.539	3.413	3.543	3.416	495.9	15.3	486.3	16.3
Tridecanoate	3.442	3.322	3.447	3.329	513.9	18.0	503.9	17.7
Myristate	3.352	3.240	3.363	3.253	530.9	17.0	521.1	17.2
Pentadecanoate	3.296	3.202	3.288	3.185	552.0	21.1	544.6	23.5
Palmitate		3.124		3.125			559.5	14.9
Heptadecanoate		3.070		3.072			577.6	18.1
Stearate		3.021		3.024			595.5	17.9
Nonadecanoate		2.982		2.980			614.7	19.2

taneous presence of a dielectrogenic group in the same chain.

Further investigations on the influence of these groups in different positions in the molecule were carried out by Kauffmann (12), who by that time had the extensive data of Dobrosserdov (4) at his disposal. He also observed the general trend in homologous series, the influence of branching, unsaturation, and substitution on the value of ϵ .

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

If we now should restrict ourselves to homologous series, we may expect better correlation using existing functions. A semiempirical additive function for homologous series was recently derived by van Elk (5), reading

$$E_m = (\epsilon - 1)^{3/4} \cdot M/d = \sum_i c_i z_i \quad [3]$$

Of interest to note is the almost analogous expression

$$P = (\epsilon - 1) \cdot 2 M/d \quad [4]$$

which is based on Jatkar's equation (11). Plotting P , the polarisation, against n , the number of carbon atoms in the molecule, Phadke (20) obtained a straight line for the normal fatty acids.

We have chosen the van Elk relation to correlate the results of our measurements because of the good fit and because of the theoretical background. In analogy to the other molar quantities 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/mole.

Saturated Fatty Acid Methyl Esters. The computed values of E_m for these compounds are included in Table III. The relative values of the molar volume, M/d , have been obtained from a previous communication (6).

The difference between two consecutive members is E_{CH_2} , the CH_2 increment. Assuming this value to be invariant within the error of measurement for the higher members of the series, the general equation relating a molar quantity to the chain length,

$$E_m = A + n E_{CH_2} \quad [5]$$

has been applied to methyl valerate and the higher homologs. Numerical values of the coefficients of the regression equation are listed in Table IV.

Comparison of the observed E_m and the values obtained from the regression equation demonstrates again the phenomenon noted in the Smittenberg relation. With a few exceptions all even numbered members of the series are lower and all odd numbered members indicate higher values than those predicted.

To determine whether alternation is really present

TABLE V
Dielectric Constant and E_m of Unsaturated Fatty Acid Methyl Esters

Compound	ϵ^{30}	ϵ^{40}	E_m^{30}	E_m^{40}
Stearate ^b			604.6	595.8
Oleate	3.211	3.117	615.0	605.3
Linoleate	3.355	3.245	631.4	619.3
Linolenate ^a	3.466	3.349	640.9	628.1
Behenate ^b			677.5	669.4
Erucate	3.043	2.956	692.0	680.8

^a Contains 27.5% *trans* double bonds.

^b Included as reference to facilitate comparison. Values obtained from data in Table IV.

or whether the deviations are just random errors of measurement we recomputed equation 5 separately for the odd and the even numbered members of the series. The results are included in Table IV. In our case \bar{n} , the average term number, of both the odd and the even series happens to be the same for each temp, i.e. \bar{n} is 10 at 20°C and 12 at 40°C. The mathematics of the statistics can now be simplified by shifting the E_m axis over \bar{n} units to the right, i.e.,

$$n' = n - \bar{n} \quad [6]$$

The estimate of the variance of a single measurement, s_y^2 , is more accurately obtained by pooling the information from both the odd and the even series, i.e.,

$$s_y^2 = \frac{(\sum E_m^2 - n' E_m - E_{CH_2} \sum n' E_m)_{\text{odd}} + (\sum E_m^2 - n' E_m - E_{CH_2} \sum n' E_m)_{\text{even}}}{m_{\text{odd}} + m_{\text{even}} - 4} \quad [7]$$

where m is the number of terms considered. The variance of the slope, s_b^2 , is obtained from

$$s_b^2 = s_y^2 / m^2 \quad [8]$$

To check whether the difference between the slopes is significant, we take this difference and divide it by its standard deviation, i.e.,

$$(E_{CH_2, \text{odd}} - E_{CH_2, \text{even}}) / \sqrt{s_b, \text{odd}}^2 + s_b, \text{even}}^2 = t \quad [9]$$

and this value is then compared to Student's t at $m_{\text{odd}} + m_{\text{even}} - 4$ degrees of freedom. The last two columns in Table IV indicate the critical values of t at the stated levels of % probability and at the stated number of degrees of freedom. The results, obtained by this method, indicate that there is no significant difference between the slopes of the two series, i.e. the two values of E_{CH_2} are essentially the same.

From equation 6 it follows that $\bar{n}' = 0$ for both the odd and even series for both temperatures. The comparison of E_m at \bar{n} is equal to the comparison of the intercepts of both these series in the shifted condition. The values of these intercepts are given in Table IV as A' . In this particular case s_a^2 , the variance of the intercept, can be computed from

$$s_a^2 = s_y^2 / m \quad [10]$$

and the difference between these two intercepts is checked for its significance by the Student's t method analogous as in equation 9.

We note from the results that at 20°C the presence of a difference is significant at the 5% critical level;

TABLE IV
Statistical Evaluation of E_m^a

Temp	Terms	A	A'	E_{CH_2}	D.F.	s_y^2	s_b^2	t_b	s_a^2	t_a	5%	1%
20C	All	277.43		18.245	9	1.78	0.016		0.16			
	Odd	278.10	460.67	18.257			0.020		0.23			
	Even	276.84	458.94	18.210		7	1.39	0.035	0.28	2.43	2.37	3.50
40C	All	266.03		18.355	13	2.02	0.007		0.13			
	Odd	267.20	487.10	18.323			0.009		0.18			
	Even	264.53	485.39	18.405		11	1.44	0.013	0.21	2.76	2.20	3.11

^a For methyl valerate and higher terms only.

at 40C this difference is still more significant. In this particular case we are, therefore, able to distinguish between two parallel running homologous series. The alternation effect is, therefore, also noted in the CH_2 increment.

Unsaturation. Although the van Elk relation has not been specifically derived for general applicability to all types of structures we were interested in the influence of unsaturation on E_m . The results are listed in Table V. Comparative saturated esters have been included to facilitate comparison. Their E_m values have been obtained from the regression equations using the data in Table IV.

The increment of the double bond apparently shows a more than proportional increase with increasing unsaturation in the same chain. This behavior has been noted earlier in other physical properties. The influence of the *trans*-modification in methyl linolenate is markedly discernible, as shown by the small difference with methyl linoleate. This might be expected as ϵ is strongly dependent on the spatial structures.

Limiting Value

The ϵ of the limiting fatty acid methyl ester may also be obtained from the following equations:

$$E_m = E_{sp} \cdot M = (\epsilon - 1)^{3/4} M/d = A + n E_{\text{CH}_2} \quad [11]$$

$$\lim_{n \rightarrow \infty} E_{sp} = \lim_{n \rightarrow \infty} (A + n E_{\text{CH}_2}) / (46.026 + n 14.026) = E_{\text{CH}_2} / 14.026 = (\epsilon_\infty - 1)^{3/4} / d_\infty \quad [12]$$

Substitution of the limiting densities obtained earlier (6), i.e. 0.85407 at 20C and 0.84225 at 40C yields

limiting dielectric constants of 2.15 at 20C and 2.14 at 40C. These values are slightly higher than those computed from the Smittenberg relation, but in view of the large amounts of extrapolation involved in both methods the fit may be considered to be reasonably close.

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A Neutron Activation Method for Soil Removal Measurements: A Comparison of the Reflectance Method and the Neutron Activation Method¹

D. A. NETZEL, C. W. STANLEY and D. W. RATHBURN,²
Midwest Research Institute, Kansas City, Missouri

Abstract

A nondestructive neutron activation analysis technique has been developed to determine the amt of particulate kaolinite clay soil removed from cotton fibers during a wash cycle.

Neutron bombardment of aluminum, present as a constituent of the kaolinite lattice structure, produces short-lived aluminum-28. The amt of particulate soil present on a piece of cotton cloth before and after the wash cycle is determined by γ scintillation counting of the aluminum-28, thus providing an absolute method for the determination of the percentage of soil removed. A comparison of this method with the reflectance method has been made, and equations relating reflectance to clay concn for washed and unwashed soiled cloths have been developed for a given surfactant. It was found that the relationship of the concn of the soil on the test cloths and the measured reflectance depends upon whether the cloth has been washed or unwashed.

The validity of the applicability of the Kubelka-Munk equation relating reflectance to soil content on cotton fabric has been experimentally confirmed for soiled cloths have high reflectivity.

Introduction

THERE HAS BEEN A large amt of work devoted to developing methods for measuring and evaluating detergency (1-3). Any true evaluation procedure for determining the detergent effectiveness of a surfactant must include a means for determining the absolute soil content on test cloths both before and after cleaning.

The method for measuring the amt of soil on a piece of cloth depends upon the type of soil being used during an investigation. Reflectance methods have been used for carbon (4), clay (5), soiled cloths and iron analyses have been used for cloth soiled with ferric oxides (2). Transmittance measurements (6) on the wash liquor have been made to determine the amt of soil removed from a cotton test swatch. With the advent of radiotracers, tagged soils of many different types have been prepared and used in the evaluation of the detergency process (7,8).

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² Kansas State University, Manhattan, Kan.