STUDIES IN THE DIELECTRIC CONSTANTS OF FATTY ACIDS*

Part II. Correlation Between the Structure and the Dielectric Constant of Fatty Acids

BY R. S. PHADKE

(Department of General Chemistry, Indian Institute of Science, Bangalore)

Several empirical equations, relating the dielectric constant with other physical properties have been reported in literature.[1] Fatty acids offer a promising field for the study of the correlation between structure and the dielectric constant.

Polar liquids are known to form association complexes by dipolar interaction. A precise knowledge of the nature and the extent of this association is of importance, as it provides a basis for correlation between the dielectric constant of a pure liquid and its electrical polarisation. In 1934, Girard[2] showed, how the effect of temperature on the dielectric constants of primary and tertiary alcohols furnishes information about association. In the case of tertiary alcohols he found that the extent of association increased with the number of carbon atoms in the molecule. Furthermore, with highly associated alcohols the dielectric constant increased with temperature, owing to the breaking up of the complexes.

There are indications that the behaviour of the fatty acids is similar to that of the tertiary alcohols. The present investigation was carried out to establish a correlation between dielectric constant and structure, in the case of fatty acids.

EXPERIMENTAL

The experimental technique was the same as employed in an earlier investigation.[3] The frequency of the quartz crystal was 1,000 Kc.

The dielectric constants of propionic, *n*-butyric, *iso*-butyric, *iso*-valeric, *n*-caproic, *iso*-caproic, caprylic, oleic, elaidic, ricinoleic and ricinelaidic acids were measured at various temperatures. Details of the preparation of samples of these acids have been given in an earlier paper.[3] Data for other acids being already available in literature, fresh measurements were deemed unnecessary.

---

* An abridged form of the thesis by the author, approved for the M.Sc. degree of the Bombay University.

In certain cases, the values of dielectric constant and polarisation were obtained by graphical interpolation.

Measurements of the densities were carried out by the specific gravity bottle method over 10° intervals and the density at the desired temperature was obtained by graphical interpolation.

Refractive indices were determined by the use of an Abbe refractometer, fitted with an efficient thermostatic control, over 10° intervals, and the refractive index at the desired temperature was obtained by graphical interpolation.

RESULTS

TABLE I. *N. Caproic Acid*

Molecular weight = 116·09

Temperature ° C.	Dielectric constant (ϵ)	Density (d)	Refractive Index (n)	Polarisation† (P) (Dimer.)
25	2·600	0·9225	1·414	402·7
30	2·608	0·9185	1·412	406·5
40	2·620	0·9100	1·408	413·3
60	2·650	0·8935	1·401	428·8
80	2·680	0·8770	*	444·8
100	2·705	0·8605	*	460·0
120	2·730	0·8440	*	475·9
140	2·750	0·8275	*	493·8
160	2·790	0·8110	*	512·5

* Refractive Indices at these temperatures could not be determined.

† Polarisation is calculated on the basis of Jatkar's Equation.

TABLE II. *Dielectric Constants of Normal Fatty Acids at 71° C.*

Acid	Number of carbon atoms (N)	Observed ϵ	Calculated ϵ	Observed ϵ/N	Calculated ϵ/N
Acetic acid[4]	2	6·600	*	3·0000	*
Propionic acid	3	3·340	3·213	1·1133	1·0550
Butyric acid	4	3·055	3·032	0·7637	0·7467
Caproic acid	6	2·665	2·796	0·4441	0·4590
Heptoic acid[5]	7	2·587	2·711	0·3695	0·3815
Caprylic acid	8	2·548	2·639	0·3185	0·3254
Palmitic acid[5]	16	2·348	2·298	0·1467	0·1417
Stearic acid[5]	18	2·318	2·245	0·1287	0·1228

* Equations (2) and (3) are not applicable to acetic acid.

TABLE III. *Relationship between the Dielectric Constant (ε) and the Molecular Weight (M) in the Homologous Aliphatic Alcohols (Girard*[2]*)*

Alcohol	Number of carbon atoms (N)	Molecular weight (M)	Dielectric constant at 20° (ε)	M × ε
Propyl alcohol ..	3	60	19·3	1160
Butyl alcohol ..	4	74	17·0	1260
Amyl alcohol ..	5	88	14·5	1275
Octyl alcohol ..	8	130	10·0	1300
Decyl alcohol ..	10	158	8·1	1280
Dodecyl alcohol ..	12	186	6·8	1265

TABLE IV. *Dielectric Constants of Aliphatic Alcohols at 20°*

Alcohol	Number of carbon atoms (N)	Observed ε	Calculated ε	Observed ε/N	Calculated ε/N
Propyl alcohol ..	3	19·3	20·5	6·433	6·845
Butyl alcohol ..	4	17·0	16·4	4·250	4·114
Amyl alcohol ..	5	14·5	13·8	2·900	2·770
Octyl alcohol ..	8	10·0	9·6	1·250	1·209
Decyl alcohol ..	10	8·1	8·1	0·810	0·813
Dodecyl alcohol ..	12	6·8	7·0	0·566	0·588

TABLE V. *Temperature Coefficients of Dielectric Constants of the Normal Fatty Acids*

Acid	Number of carbon atoms (N)	Observed $\frac{d\epsilon}{dt} \times 10^4$	Calculated $\frac{d\epsilon}{dt} \times 10^4$
Acetic acid[4] ..	2	96·66	Eqn. not applicable
Propionic acid ..	3	46·67	48·19
Butyric acid ..	4	30·00	33·07
Caproic acid ..	6	13·32	15·57
Caprylic acid ..	8	6·11	7·33
Capric acid[8] ..	10	4·00	3·45

TABLE VI. *Dielectric Constants at* 100° *of Saturated and Unsaturated Fatty Acids*

Acid	Number of carbon atoms	Iodine value	Dielectric constant at 100° C.
Stearic acid[8] ..	18	0	2·205
Oleic acid ..	18	90·0	2·485
Linoleic acid[7] ..	18	181·0	2·619
Ricinoleic acid ..	18	85·0	3·547

TABLE VII. *Dielectric Constants of the Cis- and Trans-Isomers at* 100° C.

Substance	Dielectric constant of	
	Cis-form	*Trans*-form
Oleic acid ..	2·485	2·480
Ricinoleic acid ..	3·547	3·520
Ethyl ricinoleate ..	3·475	3·775

TABLE VIII. *Polarisations of Normal Fatty Acids at* 80° *C.*

Acid	Number of carbon atoms (N)	Observed value of P	Calculated value of P
Acetic acid[4] ..	2	732·8	Eqn. not applicable
Propionic acid ..	3	378·6	382·9
Butyric acid ..	4	405·7	405·9
Caproic acid ..	6	444·8	452·1
Caprylic acid ..	8	517·6	498·2
Capric acid[8] ..	10	540·4	544·3
Stearic acid[8] ..	18	725·8	728·8

DISCUSSION

Dielectric Constants of the Normal Fatty Acids.—As typical of the fatty acids, values for the dielectric constants and other physical properties of *n*-caproic acid at various temperatures are given in Table I. The dielectric constants of other fatty acids, at various temperatures, are plotted in Fig. 1.

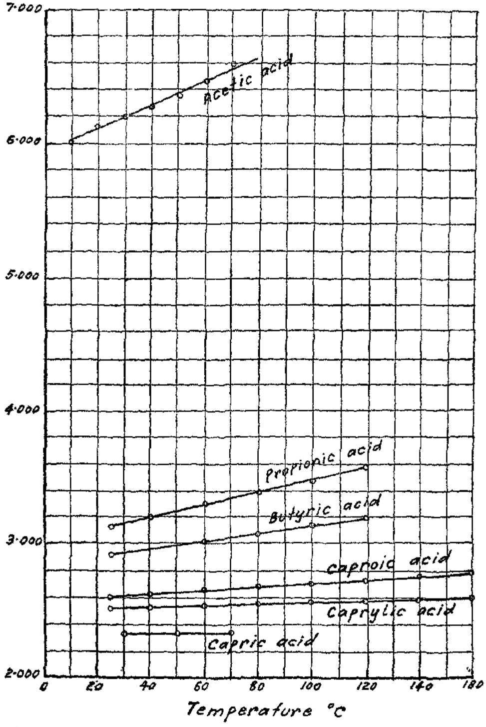

FIG. 1. Variation of Dielectric Constant of Fatty Acid with Temperature

It can be seen that the dielectric constants of the fatty acids vary linearly with temperature. The slopes of the straight lines indicate that the temperature coefficient of dielectric constant of the various fatty acids decreases with an increase in the molecular weight of the acid. In Table II the dielectric constants of normal fatty acids at 71° C. are given. It will be noticed that the dielectric constants of the fatty acids decrease with an increase in the molecular weight. Attempts have been made by the present author to establish a correlation between the number of carbon atoms and (*a*) the dielectric constant and (*b*) the temperature coefficient of the dielectric constant.

Relationship Between the Dielectric Constant (ϵ) *and the Number of Carbon Atoms* (*N*) *in the Molecule*.—For the derivation of a relationship, the dielectric constants of the acids were plotted against the number of carbon atoms in their molecules. It was found that the dielectric constants of all, except acetic acid, lay on a smooth curve. The nature of the curve indicated that the relationship between ϵ and N should be of the type $\epsilon \times \mathrm{N}^{k} = \mathrm{Z}$, where k and Z are constants.

In order to find the values of k and Z, the logarithms of ϵ/N and N were plotted. It was found that $\log_{10} \epsilon/\mathrm{N}$ varied linearly with $\log_{10}\mathrm{N}$. The equation for this straight line was found by the statistical method of least squares. The equation was

$$\log_{10} \epsilon/\mathrm{N} = 0{\cdot}5963 - 1{\cdot}2010 \log_{10}\mathrm{N} \tag{1}$$

$$\therefore\ \epsilon/\mathrm{N} = 3{\cdot}948 \times \mathrm{N}^{-1{\cdot}2010} \tag{2}$$

or

$$\epsilon \simeq 4/5\sqrt[5]{\mathrm{N}} \tag{3}$$

Thus $k = .1/5$ and $\mathrm{Z} = 4$.

In Table II, the calculated values of ϵ/N and ϵ, on the basis of equations (2) and (3) respectively, are compared with the observed values and plotted in Figs. 2 and 3.

The agreement between the observed and the calculated values of ϵ/N was statistically tested by means of the χ^2 test[6] and was found to be satisfactory. It may therefore be stated, that the relationship between the dielectric constant of a normal fatty acid and its molecular weight is expressed by the empirical relationship:

$$\epsilon \simeq 4/\sqrt[5]{\mathrm{N}}$$

The data for the dielectric constant of formic acid (in the liquid state) at various temperatures are not available. The dielectric constant of formic acid at 18·5° C. has been reported to be 47·9.[9] Calculations based on this value show that equations (2) and (3) are not applicable to formic acid.

Girard[2] has worked out the relationship between dielectric constants and molecular weights for a homologous series of aliphatic alcohols. He

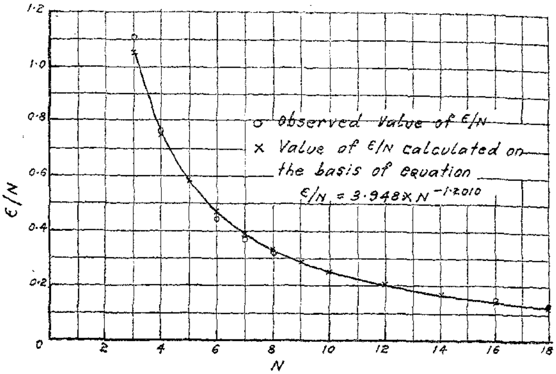

FIG. 2. Relationship Between Dielectric Constant Ratio [ϵ/N] and No. of Carbon Atoms in Fatty Acids.

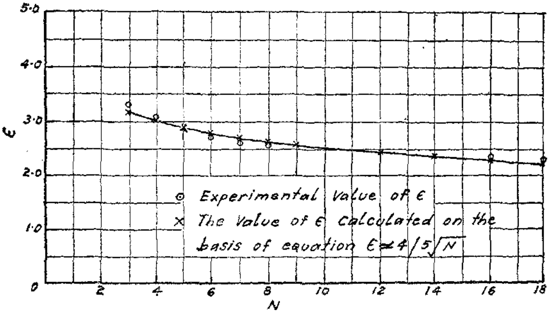

FIG. 3. Relationship Between Dielectric Constant [ϵ] and No. of Carbon Atoms in Fatty Acid.

finds that $M \times \epsilon$ is nearly constant (Table III). However, there are comparatively large divergences (about 12%) in the values, with an increase in the molecular weight.

The statistical method was applied to the experimental data of Girard[8] and the following equation was obtained.

$$\log_{10} \epsilon/N = 1 \cdot 6792 - 1 \cdot 7681 \log_{10} N \qquad (4)$$

From this equation we get:

$$\epsilon/\mathrm{N} = 47\cdot77\times \mathrm{N}^{-1\cdot7681} \tag{5}$$

$$\epsilon = 47\cdot77\times \mathrm{N}^{-0\cdot7681} \tag{6}$$

$$\epsilon \simeq 47\cdot77/\sqrt[5]{\mathrm{N}^4} \tag{7}$$

The values of ϵ/N and ϵ, calculated on the basis of equation (6), are given in Table IV. Equation (6) has been statistically tested by the χ^2 test. The agreement between the observed and the calculated values is satisfactory. The divergence is in general 4% but for propyl alcohol the divergence is 6·5%. The equation formulated above furnishes therefore, a better relationship between ϵ and N than that proposed by Girard.[2]

Correlation Between the Temperature Coefficient of the Dielectric Constant and the Number of Carbon Atoms in the Molecule of a Normal Fatty Acid.—The slopes $(d\epsilon/dt)\times 10^4$ of the straight lines in Fig. 1 are given in Table V. These values were plotted against the number of carbon atoms. It was found that the values for all, except acetic acid, lay on a smooth curve. The following equation for this curve was obtained by the method of least squares:

$$(d\epsilon/dt)\times 10^4 = 0\cdot01492\times e^{-0\cdot3767\,\mathrm{N}} \tag{8}$$

where N is the number of carbon atoms in the molecule of the fatty acid.

The calculated and the observed values of the temperature coefficients are given in Table V. The agreement, as tested by the χ^2 test, is satisfactory.

It can be seen from Fig. 1 that the dielectric constants of the fatty acids increase with rise in temperature. This is due to the breaking up of the complexes, as in the case of tertiary alcohols. The temperature coefficient of dielectric constant decreases with an increase in the number of carbon atoms, indicating that association in this homologous series decreases with an increase in the molecular weight of the acids.

Dielectric Constants of the Normal and Iso-Fatty Acids.—In Fig. 4, the dielectric constants of normal fatty acids—butyric and caproic—are plotted against temperature. In the same graph the dielectric constants of iso-butyric and iso-caproic acids are also plotted for comparison. It can be seen from Fig. 4 that a normal acid has got a higher dielectric constant than an iso-acid. However, the difference between the dielectric constants of butyric and iso-butyric acids is very marked, as compared with the difference between the constants for normal and iso-caproic acids. This shows that as the molecular weight increases in this series, the difference between the dielectric constants of the normal and the iso-acids decreases.

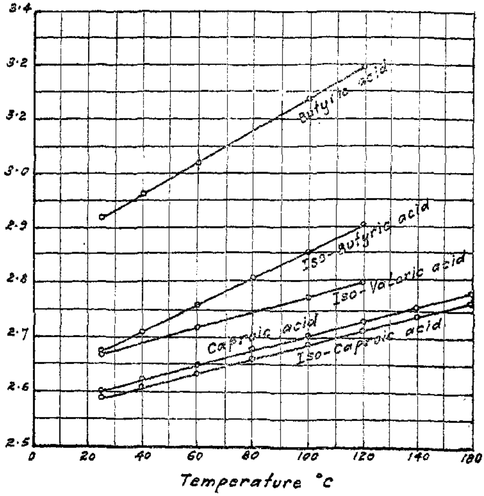

FIG. 4. Variation of Dielectric Constant of Normal and Iso-Fatty Acids with Temperature

In Fig. 4, the dielectric constants of three iso-acids, namely, iso-butyric, iso-caproic and iso-valeric acids are plotted against temperature. It will be noticed that at a given temperature, the values for the dielectric constants of the various iso-acids decrease, as the number of carbon atoms in the molecule increases. The temperature coefficient of dielectric constant also decreases with an increase in molecular weight. This behaviour is similar to that of normal acids.

Effect of Unsaturation and of the Hydroxy Group on the Dielectric Constant of Fatty Acids.—Table VI and Fig. 5 show the effect of unsaturation and of the hydroxy group on the dielectric constant of an acid containing 18 carbon atoms in its molecule. If a double bond is introduced in the molecule of stearic acid (to give oleic acid), there is an increase in the value of the dielectric constant. Similarly when two double bonds are introduced in the molecule to furnish linoleic acid, there is a further increase in the value of the dielectric constant. With the introduction of a hydroxy group in the molecule of oleic acid (togive ricinoleic acid), the dielectric constant, which is 2·485 for oleic acid, rises to 3·547.

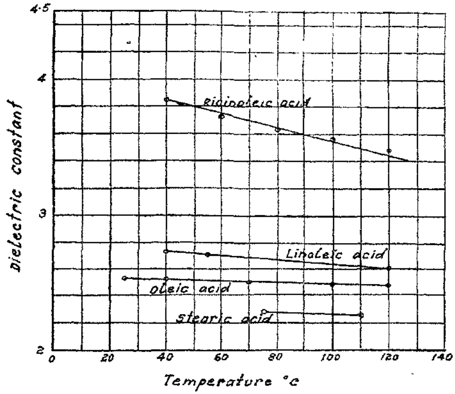

FIG. 5. Variation of Dielectric Constant of Saturated and Unsaturated Fatty Acids with Temperature

It is to be noted that the introduction of a hydroxy group in the molecule has a far more pronounced effect on the dielectric constant than the introduction of double bonds. This may be attributed to the fact that the bond moment of a double bond is very much less than that of the hydroxy group.

Effect of Elaidinization on the Dielectric Constant.—It can be seen from Table VII that the dielectric constants of the cis- and the trans-oleic acids are practically the same. In the case of ricinoleic and ricinelaidic acids however, the trans-isomer has a slightly lower dielectric constant. In ethyl ricinoleate, the trans-isomer has a much higher dielectric constant. This is obviously due to the introduction of the ethyl group in place of the hydrogen of the acid. This difference has also been noticed by the author in the dipole moments of these two substances. The *cis*-form has a moment 1·9 D as against 2·1 D of the *trans*-form.

Polarisation of the Normal Fatty Acids.—Values for the polarisations of the normal fatty acids, calculated on the basis of Jatkar's equation

$$P = (\epsilon - 1) \times 2M/d$$

at 80° are given in Table VIII. On plotting the polarisation P against N (the number of carbon atoms in the molecule) we get a straight line. The polarisation value of acetic acid, being abnormally high (710·8), does not lie on this line. The equation for the straight line, by the statistical method of least squares is

$$P = 313{\cdot}742 + 23{\cdot}0621\,N \qquad (9)$$

The polarisation values calculated on the basis of equation (9) are compared with the experimental values in Table VIII. The maximum deviation noticed is 4%. χ^2 test showed a good agreement between the observed and the calculated values.

The linear variation of P with N shows that in the homologous series of fatty acids, P is an additive property, the value for each $-CH_2-$ group being 23·0 c.c. Formic and acetic acids as already stated, are exceptions in keeping with the well-known fact that the first two members of a homologous series have, in general, abnormal properties.

The author desires to thank Dr. S. K. K. Jatkar for suggesting the problem and for the kind loan of his apparatus.

The author is indebted to Dr. B. Sanjiva Rao for his keen interest in the progress of this work and for valuable guidance in the preparation of this paper for publication.

Thanks are also due to Mr. P. Ramaswamy Ayyar, Dr. M. R. A. Rao and Mr. M. C. Satyanarayana for helpful suggestions.

REFERENCES

1.	R. J. W. Le Fevre (Book) ..	*Dipole Moments*, 1948, p. 2.
2.	Girard ..	*Trans. Farad. Soc.*, 1934, **30**, 763.
3.	Phadke, R. S. ..	*J. Indian Inst. Sci.*, 1952, **34**, No. 3, 189.
4.	Böttcher ..	*Physica*, 1939, **6**, 59.
5.	Hrynakowski and Zochowski ..	*Ber.*, 1937, **70**, 1739.
6.	Kendall, M. G. (Book) ..	*The Advanced Theory of Statistics*, 1948, **1**, 428.
7.	Stepanenko and Novikova ..	*Acta. Physico. chim.*, 1945, **20**, 653.
8.	Kulkarni, S. B. ..	Paper under publication.
9.	*International Critical Tables*, 1926, Vol. VI, p. 83.	