# STUDIES IN THE DIELECTRIC CONSTANTS OF FATTY ACIDS*

## Part IV :—Dipole Moments of Cis- and Trans- forms of Monocarboxylic Acids

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The dipole moments of the cis- and trans- isomers of fatty acids present an interesting subject of study. In this paper, investigations pertaining to the isomers of oleic and ricinoleic acids are described.

### Experimental

The experimental technique employed has been described earlier. [1, 6, 7].

Measurements of the densities were carried out with a specific gravity bottle fitted with a thermometer.

Refractive indices were determined using an Abbe refractometer, provided with an efficient thermostatic control.

*Calculation of Dipole Moment.*—The dipole moments were calculated on the basis of Jatkar's equation[9]

$$(\epsilon - n^2) \times \frac{M}{d} = \frac{4\pi N \mu^2}{kT} = P_2 - P_E$$

$P_2$ the molecular polarisation of the solute was calculated by the extrapolation method described by Jatkar[8].

$P_E$, the electronic polarisation of the solution was calculated by Jatkar's[9] formula

$$P_E = (n^2 - 1) \times \frac{M}{d}$$

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

Values at 25°C. of refractive index and density of the pure substance were employed. It was assumed that $P_E$ remained constant over the temperature range 25°-40°C.

The symbols used in the above equations have the usual meaning.[1]

## Results

In Table I are presented the experimental data on which is based the calculation of the dipole moment of ricinoleic acid in dioxane solution. Values for dipole moments for the acids investigated are given in Table II.

### Table I*

*Dipole moment of ricinoleic acid in dioxane*

| $W_2$ (Ricinoleic acid). | Solvent Dioxane at 25°C. $\epsilon_{1\cdot2}$ | 25°C. $d_{1\cdot2}$ | 40°C. $\epsilon_{1\cdot2}$ | 40°C. $d_{1\cdot2}$ |
|---|---|---|---|---|
| 0.00000 | 2.236 | 1.0277 | 2.206 | 1.0127 |
| 0.03003 | 2.268 | 1.0257 | 2.235 | 1.0113 |
| 0 04247 | 2.275 | 1.0250 | 2.251 | 1.0099 |
| 0.05751 | 2.296 | 1.0242 | 2.265 | 1.0090 |
| 0.06997 | 2.313 | 1.0231 | 2.280 | 1.0083 |
| 0.08150 | 2.320 | 1.0225 | 2.292 | 1.0074 |

| t°C. | α | β | $P_2$ | $P_E$ | $\mu \times 10^{-18}$ Jatkar (Monomer). |
|---|---|---|---|---|---|
| 25 | 1.06 | —0.065 | 1070.5 | 367.5 | 1.94 |
| 40 | 1.02 | —0.060 | 1039.8 | 367.5 | 1.95 |

* α=The slope of the straight line obtained when $\epsilon_{1\cdot2}$ is plotted against $W_2$.
β=The slope of the straight line obtained when $d_{1\cdot2}$ is plotted against $W_2$.

## Table II

*Dipole moments of the unsaturated fatty acids*

| Acid | Temp.—° C. | Solvent. | $\mu \times 10^{-18}$ Jatkar (Monomer). |
|---|---|---|---|
| Oleic acid | 25 | Dioxane | 1.73 |
| | 40 | Dioxane | 1.75 |
| Elaidic acid | 25 | Dioxane | 1.72 |
| | 40 | Dioxane | 1.72 |
| Ricinoleic acid | 25 | Benzene | 1.77 |
| | 40 | Benzene | 1.81 |
| | 25 | Petrol | 1.75 |
| | 40 | Petrol | 1.80 |
| | 25 | Dioxane | 1.94 |
| | 40 | Dioxane | 1.95 |
| Ricinelaidic acid | 25 | Dioxane | 1.99 |
| | 40 | Dioxane | 2.00 |

## Discussion

*Dipole moments of Oleic and Elaidic Acids.*—In 1938, Paranjpe and Davar[10] measured the dipole moment of oleic acid in benzene at 30° and obtained a value of 1·009D. They found that the molecular polarisations of the benzene solutions varied linearly with concentration. Volarovich and Stepanenko[11] (1940) got a value of 1.452D from a similar study of benzene solutions at 2° C. Stepanenko[12] (1944) studied the solutions of oleic acid in various solvents at 18° C. The values obtained by him were 1.22D in hexane, 1.13D in cyclohexane and 1.09D in methyl cyclohexane. From cryoscopic observations he concluded that oleic acid was associated in benzene and in cyclohexane.

Volarovich and Stepanenko[13] (1944) studied the dioxane solutions of oleic acid in concentrations varying from 0 to 1.0 molar and found the moment of the acid to be 1.68D. They concluded that oleic acid was partly associated in dioxane also. In 1947, Stepanenko, Agranat and Yakovlev[14] studied the dielectric constants of cyclohexane solutions of the acid at different temperatures and concentrations. They found that the dipole moment of the acid increased with a rise in temperature, and attributed this to association.

It will be noticed from the above data that there is considerable difference in the values of dipole moments as obtained by various workers. Marked differences are noticed with other fatty acids also. A striking example is that of acetic acid as can be seen from the data presented in Table III.

**Table III**

*Dipole moment of Acetic Acid*

| Investigator | D.C.M. Equation | Solvent |
|---|---|---|
| Wolf[2] | 0.74 | Benzene |
| Briegleb[3] | 1.04 (Dimer) | Benzene |
| Pohl[4] | 1.63 | Benzene |
| Piekara[5] | 0.38 | Heptane |
| Pohl[4] | 1.5 | Heptane |

In the opinion of the present author, the variations are due to the following causes:

(*i*) In calculating dipole moments, many of the workers have ignored the association of the acids in the different solvents.

(*ii*) Dipole moments should be independent of temperature, but owing to the association of the fatty acids, temperature affected the values.

(*iii*) Previous workers employed Debye-Clausius-Mosotti equation and obtained the value of polarisation, at infinite dilution, by extrapolation. The accuracy of such extrapolation depends on the determination of dielectric constants in highly dilute solutions. Several workers, however, employed solutions of only moderate dilution.

Published work on oleic acid indicated that the acid was not much associated in dioxane. Volarovich and Stepanenko[18] used solutions in dioxane, varying in strength from 0 to 30%. As the association effects would be greater in concentrated solutions in dioxane, the present author used solutions below 10% in strength, for determining the dipole moments of oleic and elaidic acids, in this solvent.

It was found that the dielectric constants and the densities of the solutions of the acids in dioxane varied linearly with concentration. The values of the dipole moments obtained are given in Table II.

It will be seen from the table that the moments at 25° and 40°C. are almost identical, indicating thereby that at the concentrations and temperatures studied association is negligible in the case of oleic and elaidic acids.

There is practically no difference between the moments of oleic acid (1·74D) and elaidic acid (1·72D). These two acids are cis- and trans- isomers respectively.

The similarity of the values of the two acids is not surprising as the molecule has no centre of symmetry.

*Dipole moments of Ricinoleic and Ricinelaidic Acids.*—Unlike other fatty acids, the dipole moments of ricinoleic and ricinelaidic acids (as determined from the dielectric constants of the pure liquids), do not increase in value with a rise in temperature.[1] This indicates that these acids are much less associated than other fatty acids. Determination of molecular weight of these acids in benzene gave the values of the order of 400 indicating only a small degree of association (molecular weight of the dimer 596). Determination of molecular weight by Rast's method did not indicate any appreciable association in the pure liquid. In the calculation of the moment therefore, these two acids have been assumed to exist as monomers.

In Table II is given the dipole moment of ricinoleic acid in various solvents, calculated on the basis of Jatkar's equation. The moments obtained from solutions in the different solvents are higher in value than 1.75D (obtained for the pure liquid). Furthermore, in benzene and petrol solutions, the moments increase in value with temperature. This indicates that in such solutions too, ricinoleic acid is slightly associated. In dioxane, however, the moment obtained is 1.94D and is independent of temperature. Therefore, 1.94D may be taken to be a reliable value for the moment of the monomer of ricinoleic acid.

The moment of ricinelaidic acid is 1.99D and is slightly higher than that of ricinoleic acid in dioxane. The value is practically independent of temperature. In pure liquid form, this acid also gives a moment of 1.75D.

The data presented in Table II indicate that the moments of oleic acid (1.74D) and elaidic acid (1.72D), are lower than those of ricinoleic acid (1.94D) and ricinelaidic acid (1.99D). This difference is due to the presence of the hydroxyl group, (which is a strongly polar group with a bond moment 1.5D) in the molecule of ricinoleic and ricinelaidic acids. The effect of the hydroxyl group in enhancing the moment has also been observed by Paranjpe and Davar in tri-ricinolein.[10]

In the above studies, in the case of ricinoleic acid, the measurements show that both in benzene and in petrol, the acid is associated. In dioxane, however, the acid is in monomeric form. Dioxane, therefore, is the most suitable solvent for the study of the dipole moments of the fatty acids.

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