STUDIES IN THE DIELECTRIC CONSTANTS OF FATTY ACIDS*

Part I. A Comparative Study of the Equations of Onsager and of Jatkar in Relation to Experimental Data on Pure Liquids

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INTRODUCTION

The dielectric properties of fatty acids have attracted the attention o a large number of workers since 1930 when Smyth and Rogers[1] measured the dielectric constants of acetic and butyric acids and concluded that the two acids formed dimers in the pure liquid state as also in benzene solutions The dimers were found to have a zero moment.

In the same year Zahn[2] measured the dielectric constant of acetic acid vapour at relatively high temperatures and under low pressures and confirmed the value obtained by Smyth and Rogers.[1] Zahn found that the momen of acetic acid increased with a rise in temperature. He at first attributed this to increased vibration of the OH group in the molecule but later concluded[3] that the change was due to the effect of temperature on the association of acetic acid molecules. He also studied the moments of formic and propionic acids. Investigations on the dipole moments of formic, acetic propionic, *n*-butyric and *iso*-valeric acids in benzene solutions, were published in 1930 by Wolf,[4] and Briegleb.[5] In calculating the dipole moments, Wolf ignored the association of the fatty acids in benzene solutions. Briegleb however assumed the formation of dimers in such solutions.

Eucken[6] (1932) attempted a correlation between the dissociation constants of certain aliphatic and aromatic acids and the corresponding electric moments, dielectric constants, Raman frequency and optical rotation Many irregularities were noticed. Semenchenko[7] noticed that the dipole moments of aliphatic acids were fairly constant while their solubility and surface activity varied appreciably. Smith[8] (1933) measured the dipole moments of higher fatty acids in benzene and concluded that the length o the carbon chain had scarcely any influence on the dipole moment of the molecules. In the same year, Higasi[9] studied the dipole moments of certain acids in various solvents and at different temperatures.

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Wilson and Wenzke[10] (1934) suggested that dioxane was the most suitable non-polar solvent for finding the moments of fatty acids. This oxygenated solvent dissociated the dimers of fatty acids into monomers. The authors measured the moments of formic, acetic, propionic and stearic acids in this solvent and noticed that the moment of the fatty acid was not dependent on the length of the hydro-carbon chain. The moments of acetic and propionic acids, in dioxane solutions, were practically identical with those reported for the vapour state by Zahn.[3] A considerable discrepancy was however noticed for formic acid in dioxane solution and in the vapour state. Piekara and Piekara[11] (1934) studied hexane solutions of acetic acid. Wilson and Wenzke[12] (1935) investigated the moments of fatty acids containing triple bonds, employing dioxane solutions and concluded that the triple bond had a pronounced effect on the moment of the carboxyl group. Gore and Briscoe[13] (1936) measured the dielectric constants of alcoholic solutions of 24 organic acids in an attempt to determine the effect of various ionogens on the apparent dielectric constant of the solutions. Piekara[14] (1936) investigated the dielectric constants of acetic, caprylic, oleic, palmitic and stearic acids in the neighbourhood of their freezing points.

Le Fevre and Vine[15] (1938) studied very dilute solutions of acetic, *n*-butyric and *n*-hexoic acids in benzene and developed a method for determining the association of acids from values of dielectric polarisation. They concluded that the dimers were not non-polar as assumed by some previous workers. Paranjpe and Davar[16] (1938) determined the moments of oleic and linoleic acids, triolein, triricinolein, and tristearin. They found that the moment of linoleic acid was higher than that of oleic acid and that the moments of the triglycerides increased in the order: tristearin, triolein, and triricinolein. Pohl, Hobbs and Gross[17] (1940) measured the dipole moments of certain aliphatic and aromatic acids in benzene and in heptane solutions. Volarovich and Stepanenko[18] determined the dielectric constants of linoleic and oleic acids and of triolein, employing the three liquids in the pure state, and found that the dielectric constants varied linearly with their iodine numbers. The moments of the three compounds were also determined, using their solutions in non-polar solvents. In the same year, Paranjpe and Deshpande[19] measured in benzene solution the dipole moments of lauric, palmitic and myristic acids, and of the triglycerides of the first two acids. The authors suggested a structure for the dimers of the fatty acids. The moments of palmitic acid and tri-hydroxy palmitic acid (aleuritic acid) were measured in dioxane solutions by Bhattacharya[20] (1942). He found that the moment of the hydroxy acid was higher than that of the palmitic acid.

Stepanenko[21] (1944) determined the moments of oleic and linoleic acids in solutions in hexane, cyclohexane and methyl cyclohexane. The polarisation of oleic and linoleic acids in hexane was found to be higher than that in other solvents. Volarovich and Stepanenko[22] (1944) found that the moments of oleic and linoleic acids and of triolein were higher in dioxane solutions than in benzene or toluene. The dipole moment of stearic acid was found by Stepanenko and Agranat[23] (1944) to be higher in dioxane than in cyclohexane. In dioxane, the moment of stearic acid was lower than the corresponding values of oleic and linoleic acids. Triolein was found to have a higher moment than tristearin, in dioxane solution. The moments of stearic, palmitic acids and their triglycerides were measured by Stepanenko, *et al.*,[24] in 1945, in benzene, cyclohexane and dioxane solutions. It was found that palmitic and stearic acids were as dimers in cyclohexane solutions while the triglycerides showed no appreciable association.

Arefev, Agranat and Kerman[25] (1947) found that there was no sudden change in the dielectric constant of palmitic acid near its melting point.

The effect of temperature on dipole moments in cyclohexane solutions was studied by Stepanenko, Agranat and Yakovlev[26] (1947). The moments of stearic and oleic acids increased with a rise in temperature. This effect was attributed to dissociation.

Using highly dilute solutions in non-polar solvents, to eliminate association, Potapenko and Wheeler[27] (1948) determined the moments of formic, acetic, propionic and butyric acids and found that their values generally agreed with those obtained by previous workers.

The moments of certain carboxylic acids were determined by Maryott, Hobbs and Gross[28] (1949) in dilute solutions in benzene. The authors noticed, in the case of aliphatic acids, a correlation between the structure of the acid and its tendency to associate.

For the calculations of the dipole moments the D.C.M. equation has generally been used. The equation is applicable only to solutions at high dilutions, and the published data have therefore been for very dilute solutions of substances in non-polar solvents. In 1936, however, Onsager[29] developed an equation applicable not only to solutions but also to pure polar liquids. Jatkar[30] in 1944 introduced an equation which, it was claimed, could be applied to polar liquids. In the present investigation, the validity of these two equations was examined experimentally by determining the dipole moments from data obtained for several liquids, in pure form. The following 16 liquids were investigated:—(1) Propionic acid,

(2) N. Butyric acid, (3) Isobutyric acid, (4) Isovaleric acid, (5) N. caproic acid, (6) Isocaproic acid, (7) Caprylic acid, (8) Oleic acid, (9) Elaidic acid, (10) Ricinoleic acid, (11) Ricinelaidic acid, (12) N. Propyl butyrate, (13) Ethyl caprylate, (14) Ethyl Ricinoleate, (15) Ethyl Ricinelaidiate, (16) Ethyl oleate.

EXPERIMENTAL

Propionic acid, N. butyric acid, isobutyric acid, isovaleric acid, caproic acid, iso-caproic acid. caprylic acid, propyl butyrate and ethyl caprylate, originally obtained from Kahlbaum, were fractionally distilled. The product was dried over phosphorous pentoxide and redistilled before use, taking suitable precautions to avoid contamination with moisture. An all-glass apparatus was employed for the distillation.

The purity of all the samples thus obtained was checked by approved methods.

Oleic Acid.—The fatty acids of groundnut oil were liberated by treating with hydrochloric acid, in hot aqueous solution, the sodium soap of the oil. The solid fatty acids present deposited on standing for several days. The acids in the liquid condition were filtered off and converted into their lead salts which were treated with petroleum ether at 15° C., to extract the lead compound of the unsaturated acids. The extract was treated with cold dilute nitric acid and from the unsaturated acids liberated, oleic acid was isolated by the procedure described by Skellon.[31] The acid was further purified by fractional distillation at 1 mm. pressure.

Elaidic Acid.—A comparative study was made of the various methods described by Griffiths and Hilditch[32] for the conversion of oleic acid into elaidic acid. The best reagent was found to be a mixture of nitric acid and sodium nitrite, used in the following way.

100 g. of pure oleic acid were mixed with 40 ml. of 15% aqueous solution of sodium nitrite in a round-bottom flask and treated at once at 30° C. with 80 ml. of 1 : 1 aqueous nitric acid and stirred for half an hour. The flask was then cooled in a mixture of ice and salt. The solidified acids were separated from the aqueous layer and washed free of mineral acid, with water. The solid product consisting of crude elaidic acid was purified by recrystallising three times from acetone at − 15° C. The elaidic acid thus purified was carefully dried *in vacuum* over phosphorus pentoxide. It had a constant melting point of 44° C.

Ricinoleic Acid.—The fatty acids of castor oil were liberated, employing the same technique as used for groundnut oil. The saturated acids present were allowed to settle down, keeping the alcoholic solution at − 20° C. for several days as described by Rider[33] and from the filtrate the barium salts of the fatty acids present were prepared. The barium salt of ricinoleic acid was isolated by taking advantage of its insolubility in cold alcohol and purified by recrystallisation. Ricinoleic acid was freshly prepared before use by the treatment of the suspension of the barium salt in ether, with hydrochloric acid. The acid does not keep well as it undergoes polymerisation.

Ricinelaidic Acid.—The treatment with sodium nitrite and nitric acid (employed for the preparation of elaidic acid from oleic acid) was utilised for the conversion of ricinoleic acid into ricinelaidic acid. The reaction however was carried out at 60°. Ricinelaidic acid was purified by the same method as was employed for elaidic acid.

Esters of Fatty Acids.—The ethyl esters of oleic, ricinoleic and ricinelaidic acids were prepared by refluxing the mixture of the acid, ethyl alcohol and sulphuric acid. The esters were purified by fractional distillation under reduced pressure.

To check the purity of the samples obtained, certain physical and chemical constants were determined and compared with the data reported in literature.

The data are given in Table I.

Measurement of the Dielectric Constant.—The apparatus employed for the measurement of the dielectric constant was essentially the same as that used by Jatkar.[37] The calibration of the cell was effected by employing pure benzene as the reference liquid. To maintain the temperature of the cell constant, a Dewar flask filled with oil was used as a thermostat. The oil was heated electrically, employing a rheostat to control the resistance of the heating coil. An accuracy of $\pm 0 \cdot 1°$ C. could be secured in the control of the temperature of the bath. In the case of pure liquids, the dielectric constants were measured at temperature intervals of 10° C. When necessary, values were obtained by graphical interpolation.

Measurement of Density.—Densities of the pure liquids were determined by the specific gravity bottle method over 10° intervals, taking suitable precautions to secure accuracy. It was found that in all the cases, the density varied linearly with temperature. Densities at desired temperatures were obtained by interpolation.

The densities of molten solids were determind by the displacement method. A small glass bulb, weighted with mercury, was suspended from the left arm of a chainomatic balance using a thin copper wire that had been

TABLE I (A)

Physical and Chemical Constants of the Fatty Acids and Esters

	Oleic acid		Elaidic acid		Ethyl oleate	
	Experimental	Reported	Experimental	Reported	Experimental	Reported
Molecular weight ..	282·5	282·3	282·3	282·0	311·0	310·0
Iodine value ..	89·97	91·0	89·95	*	81·5	*
Melting point [°C.] ..	13°	13–14°	44°	44–45°	†	*
Boiling point [°C.] .	195–7° (1 mm.)	203·5°$^{\lambda}$ (5 mm.)	†	234° (15 mm.)	175° (4 mm.)	216–17° (151 mm.)
Density ..	$D^{20^\circ}_{4^\circ}$ 0·902	$D^{20^\circ}_{4^\circ}$ 0·898$^{\lambda}$	$D^{79\cdot4^\circ}_{0^\circ}$ 0·8527	$D^{79\cdot4^\circ}_{0^\circ}$ 0·8505	$D^{25^\circ}_{4^\circ}$ 0·8661	$D^{25^\circ}_{4^\circ}$ 0·8671
Refractive index ..	$n^{20^\circ}_{D}$ 1·461	$n^{20^\circ}_{D}$ 1·461	$n^{44^\circ}_{D}$ 1·450	$n^{100^\circ}_{D}$ 1·431	$n^{25^\circ}_{D}$ 1·449	*
REFERENCES :		Skellon[31] $^{\lambda}$Heilbron [34]		Heilbron[34]		Heilbron[34]

* Not reported. † Not determined.

TABLE I(B)

Physical and Chemical Constants of the Fatty Acids and Esters

	Ricinoleic acid		Recinelaidic acid		Ethyl Ricinoleate		Ethyl Ricinelaidiate	
	Experimental	Reported	Experimental	Reported	Experimental	Reported	Experimental	Reported
Molecular weight ..	299·0	298·0	298·5	298·0	326·0	326·0$^{\lambda}$	326·5	326·0
Iodine value ..	88·76	88·52	86·0	*	78·0	77·92	77·91	*
Acetyl value ..	138·0	137·9	138·5	*	*	*	†	*
Melting point [°C.] ..	†	5·5°	52–53*	51–52°	*	*	18°	16°
Boiling point [°C.] ..	†	*	†	240–2° (10 mm.)	206–8° (5–6 mm.)	206° (5–6 mm.)	204° (4 mm.)	*
Density ..	$D^{27\cdot4^\circ}_{4^\circ}$ 0·940	$D^{27\cdot4^\circ}_{4^\circ}$ 0·940	$D^{53^\circ}_{4^\circ}$ 0·9280	*	$D^{20^\circ}_{0^\circ}$ 0·9120	$D^{20^\circ}_{0^\circ}$ 0·9182	$D^{25^\circ}_{4^\circ}$ 0·9110	*
Refractive index ..	$n^{20^\circ}_{D}$ 1·471	$n^{20^\circ}_{D}$ 1·471	$n^{53^\circ}_{D}$ 1·462	*	$n^{25^\circ}_{D}$ 1·460	$n^{25^\circ}_{D}$ 1·460	$n^{25^\circ}_{D}$ 1·459	*
Optical activity $(\alpha)_D$	+6·3	+7·15	+6·4	+6·67	+5·0	+5·28	+5·1	*
REFERENCES :		Brown and Green[35]		Heilbron[34]		Brady[36] $^{\lambda}$Heilbron[34]		Heilbron[34]

* Not reported. † Not determined.

silver plated. The density of the molten solid was obtained by immersing in it the glass bulb and reading the balance. The thermostatic arrangement described above was employed for temperature control.

Measurement of Refractive Index.—An Abbe Refractometer, fitted with an efficient thermostatic control, was employed when necessary, the refractive index was obtained by interpolation.

CALCULATION OF DIPOLE MOMENT

The following equation of Onsager[29] was used to calculate the dipole moments from data of pure liquids:

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon (n^2 + 2)^2} \cdot \frac{M}{d} = \frac{4\pi N\mu^2}{9kT}$$

where ϵ = dielectric constant of liquid at T°.

d = density of liquid at T°.

n = Refractive index of liquid at T°.

N = Avogadro number $= 6{\cdot}06 \times 10^{23}$.

k = Boltzmann Constant $= 1{\cdot}39 \times 10^{-16}$.

M = Molecular weight.

T = Temperature on the absolute scale.

P = The total polarisation.

Values for the dipole moments from data of pure liquids were also determined by applying the following equation of Jatkar:[30]

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

$$P = (\epsilon - 1) \cdot \frac{M}{d}.$$

Electronic Polarisation (P_E).—In calculating P_E at temperature T°, the experimental values actually obtained for the refractive index and the density at T°, were employed. Jatkar's[30] formula for P_E is:

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

In calculating the dipole moment, P_E was assumed to be constant,

RESULTS

TABLE II

Dipole Moments of Esters

Temperature °C.	Propyl butyrate		Ethyl caprylate		Ethyl oleate		Ethyl ricinoleate		Ethyl ricinelaidiate	
	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager
	(Monomer)		(Monomer)		(Monomer)		(Monomer)		(Monomer)	
25	1·47	1·73	1·40	1·67	1·52	1·81	1·93	2·23	2·15	2·47
30	1·47	1·74	1·41	1·68	1·53	1·82	1·93	2·23	2·15	2·47
40	1·48	1·75	1·41	1·70	1·54	1·85	1·93	2·25	2·15	2·49
60	1·49	1·79	1·43	1·73	1·57	1·90	1·93	2·27	2·14	2·49
80	1·50	*	1·43	*	1·59	*	1·91	*	2·11	*
100	1·50	*	1·43	*	1·60	*	1·89	*	2·07	*
120	1·49	*	1·42	*	1·60	*	1·85	*	2·02	*

* Not calculated as refractive index at these temperatures could not be determined.

TABLE III

Dipole Moments of Unsaturated Fatty Acids

Temperature °C.	Oleic acid		Elaidic acid		Ricinoleic acid		Ricinelaidic acid	
	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager
	(Dimer)		(Dimer)		(Monomer)		(Monomer)	
25	1·1	1·43	†	†	1·75	2·02	†	†
30	1·18	1·44	†	†	1·75	2·02	†	†
40	1·20	1·48	1·25 (at 44°)	1·54	1·75	2·02	1·76 (at 53°)	2·06
60	1·29	1·51	1·29	1·60	1·75	2·05	1·74	*
80	1·38	*	1·34	*	1·78	*	1·76	*
100	1·43	*	1·39	*	1·79	*	1·78	*
120	1·48	*	1·44	*	1·81	*	1·80	*

* Not calculated as refractive index at these temperatures could not be determined.

† The substances are solids at these temperatures.

TABLE IV (A)

Dipole Moments of Saturated Fatty Acids

(Variation with temperature)

Temperature °C.	Propionic acid		Butyric acid		Iso-butyric acid		Iso-valeric acid	
	$\mu \times 10^{-18}$ Jatkar (Dimer)	$\mu \times 10^{-18}$ Onsager (Dimer)	$\mu \times 10^{-18}$ Jatkar (Dimer)	$\mu \times 10^{-18}$ Onsagar (Dimer)	$\mu \times 10^{-18}$ Jatkar (Dimer)	$\mu \times 10^{-18}$ Onsager (Dimer)	$\mu \times 10^{-18}$ Jatkar (Dimer)	$\mu \times 10^{-18}$ Onsager (Dimer)
25	0·98	1·22	0·98	1·22	0·86	1·08	0·91	1·14
30	1·00	1·25	1·00	1·24	0·88	1·10	0·93	1·16
40	1·01	1·31	1·04	1·30	0·92	1·16	0·96	1·21
60	1·14	1·43	1·13	1·33	1·00	1·33	1·03	1·31
80	1·23	*	1·21	*	1·08	*	1·10	*
100	1·33	*	1·30	*	1·16		1·18	*
120	1·43	*	1·38	*	1·24	*	1·25	*

* Not calculated as refractive index at these temperatures could not be determined.

TABLE IV (B)

Dipole Moments of Saturated Fatty Acids

(Variation with temperature)

Temperature °C.	Caproic acid		Iso-caproic acid		Caprylic acid	
	$\mu\times10^{-18}$ Jatkar	$\mu\times10^{-18}$ Onsager	$\mu\times10^{-18}$ Jatkar	$\mu\times10^{-18}$ Onsager	$\mu\times10^{-18}$ Jatkar	$\mu\times10^{-18}$ Onsager
	(Dimer)		(Dimer)		(Dimer)	
25	0·90	1·12	0·90	1·12	0·91	1·14
30	0·92	1·15	0·92	1·15	0·93	1·16
40	0·95	1·23	0·95	1·19	0·96	1·20
60	1·03	1·30	1·02	1·29	1·02	1·30
80	1·11	*	1·09	*	1·09	*
100	1·18	*	1·17	*	1·16	*
120	1·26	*	1·24	*	1·23	*
140	1·34	*	1·31	*	1·30	*
160	1·42	*	1·41	*	1·38	*

* Not calculated as refractive index at these temperatures could not be determined.

TABLE V*

Dipole Moment of Acetic Acid at Various Temperatures

Temperature °C.	$\mu \times 10^{-18}$ Jatkar	$\mu \times 10^{-18}$ Onsager
	(Dimer)	
10	1·55	1·83
20	1·60	1·90
30	1·65	1·95
40	1·70	2·00
50	1·76	2·10
60	1·82	2·17
80	1·97	2·37

* Data from Bottcher.[48]

Values for the dipole moments of capric and stearic acids at different temperatures as reported by Miss S. B. Kulkarni[47] on the basis of dimers employing Jatkar's equation are as follows:

Capric acid: 31·5° C. 0·73; 50° C. 0·80; 70° C. 0·86 D.

Stearic acid: 68° C. 0·93; 75° C. 1·00; 80° C. 0·61; 100° C. 0·71; 110° C. 1·07 D.

DISCUSSION

The data presented in Tables II, III, IV and V show that in calculating the dipole moments of fatty acids, their molecules are to be considered to be dimers.

It has long been known that fatty acids are in the form of dimers in the solid, the liquid and the gaseous state, as well as in solution. Vapour density measurements by Fenton and Garner[38] and by Coolidge[39] have furnished ample proof of the existence of aggregates of fatty acids, in the gaseous state. Molecular weight and partition coefficient data obtained by Beckmann,[40] Trautz and Moschel,[41] and Herz and Fischer[42] indicate that fatty acids are present as dimers, when in solution. X-Ray investigations by Muller[43] have shown that in the solid state, higher fatty acids are paired. A similar conclusion has been drawn by Morrow[44] by an X-ray study of the fatty acids in the liquid condition.

Owing to the non-applicability of the D.C.M. equation to pure liquids, earlier workers could not correlate dipole moments with dielectric constants, in the case of polar liquids. The enunciation of Onsager's[29] theory, however, rendered such correlation possible; and Böttcher[48] showed that with many liquids, the values of dipole moments calculated from Onsager's equation agreed with those obtained on the basis of the D.C.M. equation which is applicable only to dilute solutions of such liquids. The dipole moments of the fatty acids have been calculated on the basis of the D.C.M. equation assuming that dimers of the acids are present in such solutions. These values of dipole moments which are reported in literature, can be compared with the values obtained on the basis of the equations of Onsager[29] and of Jatkar[30] for the pure polar liquids, making use of the data obtained by the present author. The molecules of pure liquids at room temperature (25° C.) may be assumed to be as dimers. The dissociation of the dimers is scarcely to be expected at room temperature.

The applicability of the two equations to polar liquids in a pure state can be examined on the basis of values given in Table VI. It will be seen from the data, that the values for moments obtained by the application of Jatkar's equation closely agree with those determined on the basis of the D.C.M. equation. Onsager's equation on the other hand, gives much higher values.

In employing Onsager's equation, Böttcher[48] also gets high values for the moments of certain associated liquids like water and ethyl alcohol. Wilson has pointed out that for associated liquids, Onsager's equation does not hold good because in deriving the equation, the possibility of molecular association in polar liquids has not been taken into account.

TABLE VI

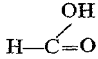
Dipole Moments of Dimers

° C.	Acid	$\mu \times 10^{-18}$ D.C.M. (A)	$\mu \times 10^{-18}$ Jatkar (B)	Deviation from D.C.M. (A − B)	$\mu \times 10^{-18}$ Onsager (C)	Deviation from D.C.M. (A − C)
30	Acetic acid ..	1·04*	1·65	−0·61	1·95	−0·91
25	Propionic acid ..	0·88*	0·98	−0·10	1·22	−0·34
25	Butyric acid ..	0·93*	0·98	−0·05	1·22	−0·29
25	Iso-valeric acid ..	0·89*	0·91	−0·02	1·14	−0·25
25	Caproic acid ..	1·0†	0·90	+0·10	1·12	−0·12
25	Caprylic acid ..	1·0†	0·91	+0·09	1·14	−0·14

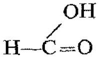
* Briegleb[5] † Le Fevre and Vine[15]

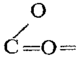
THE STRUCTURE OF DIMERS

The association of the fatty acids to form dimers is a typical instance of anti-parallel association, in which the moments of the monomers are only partially counterpoised. The manner in which dimers of the acids are formed from the monomers has been a controversial subject as can be realised from the following brief review.

According to Zahn,[3] in the dimers of formic acid, the two  $H—\overset{OH}{\overset{/}{C}}=O$ planes are approximately perpendicular to each other. The four oxygen atoms from the two molecules of formic acid form a rectangle whose plane is perpendicular to the other two planes. Zahn has presumed that the two molecules are held together by hydrogen bonds.

Zahn calculated the electric moment to be 1·1 D for the dimer of formic acid. This value compares favourably with 0·99 D obtained by him experimentally.

The electron diffraction investigations by Bru and Hengstenberg lead to a slight modification of the structure postulated by Zahn.[45] The alteration consists in placing the four oxygen atoms at the corners of a tetrahedron. Pauling and Brockway[46] state however that this new model is not in agreement with the electron diffraction patterns obtained by them for the acid. Pauling and Brockway have therefore, suggested a new model for the dimers of formic acid in which the two  $H—\overset{OH}{\overset{/}{C}}=O$ molecules lie in a common plane and are held together by two hydrogen bonds. In this structure, the distance C—O is 1·29 ± 0·02 Å and the O—C—O angle is 125 ± 5°.

The structure suggested by Pauling and Brockway[46] is symmetrical and therefore, should possess no moment. As the dimers of the fatty acids show a significant moment, the symmetrical plane structure indicated by Pauling and Brockway cannot be considered to be satisfactory. Paranjpe and Deshpande[19] have therefore suggested a spatial structure for the higher fatty acids in which the H atoms of the COOH group of one molecule of the fatty acid is chelated to the oxygen of the other molecule in the dimer. In this structure, the angles are:  $\overset{O}{\overset{/}{C}}=O=125°$, O—H—O = 180° and H—C—O = 110°. Paranjpe and Deshpande have stated that the only effective moments in this structure are the two bond moments C=O and C—O which are 2·3 D and 0·7 D respectively. The resultant of these two moments is 1·99 D and the authors suggest that the moment of the dimer depends upon the angle between the two resultants. On the assumption that the moment of the dimer is 0·78 they have calculated this angle to be 117°. There seems to be an error in this calculation for a recalculation by the present author indicates the correct value to be 157°. The data in Table VI show that the moment is 0·9 D. This gives a value of 154° for the angle. Calculations on the basis of a value of 154°, show that the bond angle  $\overset{O}{\overset{\diagup}{C}}{=}O$ is 122°. This agrees fairly well with the value 125 ± 5° obtained by Pauling and Brockway.[46]

EFFECT OF TEMPERATURE ON DIPOLE MOMENT

Dipole Moments of Monomers of Saturated Fatty Acids.—Zahn[3] measured the dielectric constants of the vapours of acetic and propionic acids at eleven different temperatures in the region of 297° K. He found that at high temperatures, the dielectric constant of the vapours varied linearly with temperature. At low temperatures, however, owing to association, the variation was not linear. Zahn assumed that at high temperatures, the errors in the calculation of the moment due to association were negligible and calculated the moments of the monomers of acetic and propionic acids from the pressure curves obtained by him at high temperatures. If there was no association, the moment should be unaffected by temperature. Zahn actually found that the moments of acetic and propionic acids were constant at temperatures above 440° K. This indicated that there was negligible association at these temperatures and that the moments 1·73 D and 1·74 D were reliable values for the moments of the monomers of acetic and propionic acids respectively. Wilson and Wenzke[10] studied the dielectric constants of the solutions of acetic and propionic acids in dioxane, and by the application of Hedestrand method calculated the moments of these acids. They assumed that in dioxane these acids were present as monomers. The dipole moment they obtained for both the acids was 1·75 D. These authors also studied the moment of stearic acid in dioxane solutions and found it to be 1·74 D; Wilson and Wenzke[10] therefore, concluded that all the fatty acids in this homologous series (with the exception of formic acid) had approximately a moment of 1·75 D. There is a large divergence between the moment obtained for formic acid from a study of the vapour (1·51 D)[3] and the value (2·07 D) obtained by Wilson and Wenzke[10] by a study of dioxane solutions. These authors have attributed the discrepancy to the high value of the dissociation constant of formic acid.

The dipole moments of the iso-acids in monomeric form have not so far been determined. A branched chain is supposed to have some influence on the dipole moment. It is therefore of interest to know the difference between the moment of an iso-acid and a normal acid. The influence of molecular weight on the moment of an iso-acid is also worthy of study.

Dipole Moments of the Dimers of the Fatty Acids.—It will be seen from Tables III to V, that the dipole moments of dimers of the fatty acids increase with a rise in temperature. This effect is due to the dissociation of the dimers.

In Fig. 1, the dipole moments of the dimers of the normal saturated atty acids (calculated on the basis of Jatkar's equation) have been plotted gainst temperature. It will be noticed that the moments vary linearly with emperature. The slopes of these straight lines, however, show a decrease vith increasing molecular weight of the acid. This indicates that the degree f association of the acids decreases with increasing molecular weight of the cid. The iso-acids also behave similarly.

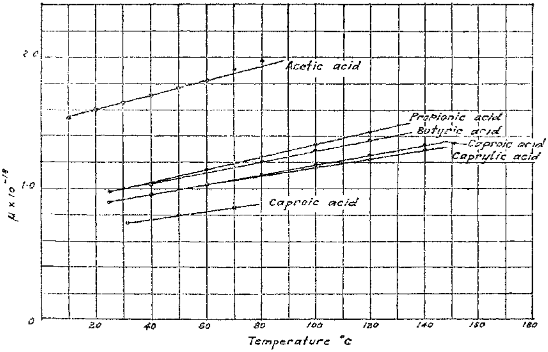


Fig. 1 VARIATION OF DIPOLE MOMENT OF NORMAL FATTY ACIDS WITH TEMPERATURE.

The dipole moments of oleic and elaidic acids also increase with rise temperature, indicating that these acids, in common with other fatty acids, re also associated. It will be seen that the dipole moments of ricinoleic nd ricinelaidic acids, however, are practically independent of temperature dicating that they are much less associated than the other fatty acids. The sters also do not show a change in moment with temperature as there is ractically no association in esters.

The following general conclusions can be drawn about the equations f Jatkar and of Onsager:

(1) In the case of an associated compound, the dipole moment depends upon the degree of association of the substance.

(2) If a compound is not associated, its dipole moment calculated on the basis of either of the equations is practically independent of temperature.

(3) The value of the dipole moment calculated according to Onsager's equation, is invariably higher than that calculated on the basis of the equation of Jatkar.

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