

The Electric Moments of Fatty Acids

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and therefore possesses definite physical significance. As a matter of fact, we may conceive of Eq. (6) representing rather closely the true conditions, as outlined early in this paper. Eq. (6), with the condition that the rate of change of concentrations in an elementary layer is zero, automatically takes care of the requirement that the rate of change of heat energy shall also be zero. The equations, however, go further in that they also impose conditions as to the flow of chemical energy among the different layers which, as pointed out, the other theories neglect.

In common with other authors our differential equation is solved by imposing a condition

regarding the temperature gradient. The type of our equation is such that its solution is imaginary if one assumes that the temperature gradient disappears at point x_b where the gas is completely burned. The solution is obtained by making the temperature gradient disappear toward the unburned side. We believe that this is in harmony with the physical picture of the theory. In their equations, Jouguet and Nusselt impose the condition that the temperature gradient disappears toward the burned side, although for mathematical purposes the same condition may be employed for the unburned side. The latter was utilized by Daniell.

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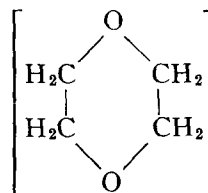
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A number of investigators have reported moments of fatty acids from dielectric constant and density measurements made upon the solutions of these substances in benzene. As is well known, fatty acids exist as double molecules when dissolved in hydrocarbons and consequently these reported moments have no significance as applied to the single molecules. No detailed reference to this work need be given. From measurements made upon the gaseous substances Zahn¹ reported moments of 1.51—, 1.73— and 1.74×10^{-18} c.g.s.e.s.u. for the simple molecules of formic, acetic and propionic acids, respectively. At the temperatures of measurement the formic acid existed as a mixture of single and double molecules. From a knowledge of the density of the gas the fraction of the molecules in the associated state was calculated and the moments of both the single and double molecules were reported. The latter was given to be 0.99 D. The moments of acetic and propionic acids were obtained from measurements made at temperatures sufficiently high that dissociation of the double molecules into single molecules was sufficiently complete.

Oxygenated solvents have the property of dissociating the double fatty acid molecules into

single ones. Nearly all of the common oxygenated solvents are polar and therefore not suited as media for measuring the moments of polar solutes. Recently dioxane



has been used in the determination of electric moments. It is non-polar and miscible with the lower acids and dissolves sufficient amounts of the higher members. The authors measured the moments of formic, acetic and propionic acids in dioxane for the sake of making comparisons with the values obtained for the gaseous substances. In order to determine the effect of greatly increasing the length of the hydrocarbon chain data are also given for stearic acid in Table I.

The polarizations at infinite dilution were calculated by the method of Hedestrand.² In Table II are listed the values of the polarization at infinite dilution, the molecular refraction for the sodium line and the electric moment.

The moments of acetic and propionic acids as

¹ C. T. Zahn, *Phys. Rev.* **37**, 1516 (1931).

² Hedestrand, *Zeits. f. physik. Chemie* **B2**, 428 (1929).

TABLE I. Dielectric constants and densities of solutions of fatty acids in dioxane. (Temp. 25°C.)

c_2	ϵ	d
Formic acid		
0.000000	2.2357	1.02771
.017432	2.3409	1.02892
.026661	2.3968	1.02969
.036226	2.4503	1.03014
Acetic acid		
0.000000	2.2357	1.02771
.021864	2.3258	1.02817
.026648	2.3443	1.02839
.034211	2.3740	1.02847
Propionic acid		
0.000000	2.2357	1.02771
.028550	2.3534	1.02714
.031317	2.3649	1.02715
.036956	2.3898	1.02706
Stearic acid		
0.000000	2.2357	1.02771
.009281	2.2713	1.02203
.014773	2.2927	1.01843
.017352	2.3005	1.01699

determined in dioxane are practically identical with those reported for the gaseous state. It will also be noted that lengthening the hydrocarbon chain has no effect on the moment of the fatty acid, the moment of stearic acid being identical with that of acetic acid. There is a considerable discrepancy between the values of the moment of formic acid obtained from measurements in dioxane and that calculated for the single molecules in the gaseous state. In order to check

TABLE II. Polarizations and moments of fatty acids.

Fatty acid	P_∞	MR_D	$10^{18} u$
Formic	90.52	8.56	2.07
Acetic	75.91	13.00	1.74
Propionic	80.78	17.50	1.75
Stearic	149.90	86.89	1.74

the work a second lot of C.P. formic acid was purchased and, as was done for acetic and propionic acids, purified by fractional crystallization followed by distilling through an efficient column. The two samples of formic acid gave the same moment.

Apparently the replacement of hydrogen of formic acid by an alkyl group results in a considerable reduction of the moment. The steric effects and the inductive effects resulting from such a substitution are too complicated to be handled quantitatively at the present state of our knowledge.

The ionization constants at 25° of formic, acetic and propionic acids are $2.1(10^{-4})$, $1.8(10^{-5})$ and $1.4(10^{-5})$, respectively. Apparently the higher electric moment of formic acid is related to its higher ionization constant. It is possible that the O—H linkage is more polar in formic acid than it is in the higher fatty acids and this is suggested as a partial explanation of the considerable difference in moment of the first and later members of the series.