DIELECTRIC PROPERTIES OF SOME VEGETABLE OILS.

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Experiments were carried out to study the dielectric properties at room temperature (26°C.) of some common vegetable oils and their dipole character has been established by studying the variation of the dielectric constant of their solution in benzene as a function of their concentration. The oils studied were: (1) Castor Oil; (2) Olive Oil; (3) Sesame Oil; (4) Cocoanut Oil. These were particularly chosen as each represents the group of oils possessing its own physical and chemical characteristics.[1] It was necessary to work on a particular sample of reliable purity and to complete the observations before it underwent any change. For each sample, measurements were made of the density, the refractive index and the dielectric constant and that sample which agreed most with the standard data in the literature was selected. Table I shows the comparative values.

Table I.

Oil	Density		Refractive index		Dielectric constant	
	(Obs.)	(Lit.)	(Obs.)	(Lit.)	(Obs.)	(Lit.)
Castor Oil	0·9612	0·960 —0·967	1·4745	1·4546	4·478	4·540
Olive Oil	0·9125	0·914 —0·920	1·4665	1·4410	3·252	3·185
Sesame Oil	0·9132	0·921 —0·924	1·4675	1·4661	3·365	..
Cocoanut Oil ..	0·9204	0·9259	1·4521	1·4295	3·254	..

A sample of Merk's extra pure crystallisable benzene was similarly experimented upon. The constants agreed well with those found in the

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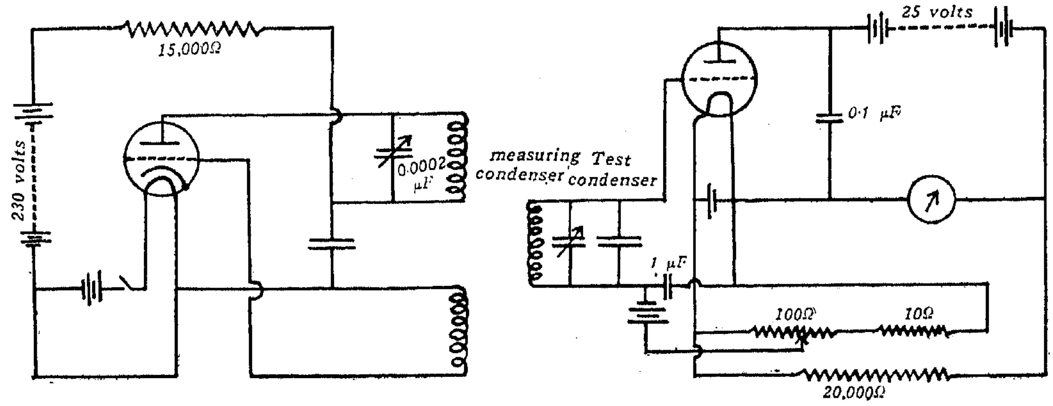
[1] "Chemical Technology and Analysis of Oils, Fats and Waxes" by Dr. Lewkowitsch, 6th Edn., 1922, II.

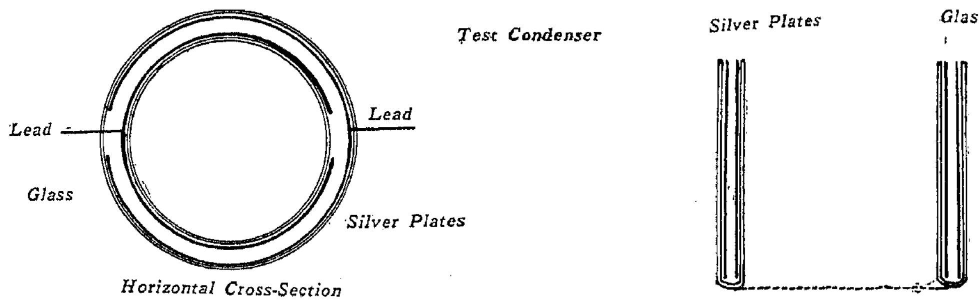
literature[2] and hence no elaborate purification of benzene was considered as of any material value in the present investigations.

Glass-stoppered bottles were used to prepare solutions of oils in benzene. The liquids were thoroughly mixed to form a clear solution. The densities were determined both by the specific gravity bottle and the pyknometer, care being taken to prevent any loss by evaporation. Simultaneously an Abbe direct reading Refractometer was used to determine the refractive index.



Oscillator *Valve Volt Meter*

Fig. 1A.



Horizontal Cross-Section *Vertical Cross-Section*

Fig. 1B.

The methods of calculating the mole fraction as well as the equations for polarization require a knowledge of the molecular weights of the oils. Further, errors in molecular weight cause differences in the calculated values of moment. The values for molecular weight available in the literature, however, widely differ.[1] The expedient adopted by Stoops[3] in a similar investigation, of calculating the molecular weight from the known composition, is at best only an approximation. It was therefore thought necessary to repeat and extend the measurements of Stoops by determining independently

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[2] (*a*) *International Critical Tables*, I, 1928.
(*b*) Smyth, *J. Amer. Chem. Soc.*, 1928, **50**, 1536.
(*c*) Williams and Krchma, *J. Amer. Chem. Soc.*, 1927, **49**, 2408.
(*d*) Hartshorn and Oliver, *Roy. Soc. Proc.*, 1929, **A123**, 664.

[3] W. N. Stoops, *J. Phys. Chem.*, 1931, **35**, 1704.

the molecular weights of the actual samples used. The cryoscopic method was adopted, using benzene as solvent, and the best mean of a number of observations for each oil, together with the values reported in the literature, are presented in Table II.

TABLE II.

	Authors F.P.Method	Normann[4]		Baker[5] F.P. Method	Held[6] F.P. Method	Stoops[3] Calculated
		Saponification Method	F.P. & B.P. Methods			
Castor Oil ..	935	904·7	834 to 1078	844 to 1031	827 to 1068	933
Olive Oil ..	830	917·0	501 to 691	803	829 to 949	..
Sesame Oil ..	848	..	..	800	..	..
Cocoanut Oil ..	638	..	..	613	..	..

The dielectric constants were determined at 30 meters (10,000 Kc.). The resonance was observed by a valve-voltmeter[7] which has the unique qualities of absorbing practically no power from the circuit and possessing low capacitance.[8] The measuring variable condenser was of 100 $\mu\mu$F capacity with a scale reading up to 0·025 of a degree and was so constructed as to satisfy all conditions for no loss at high frequencies. It was calibrated *with the leads, etc.*, by means of a standard variable air condenser.

The test condenser had a capacity of 4·500 cms. and was designed of two silver plates bent cylindrically and fixed between the two walls of a Dewar's flask which was cut at its base and inverted. The thickness of the plates was such that the elasticity was sufficient to keep the plates in position without any support. The capacity of the very short and fixed leads connecting this condenser to the measuring condenser was taken into account while calibrating the latter. Only a small quantity was sufficient to fill the condenser so that the plate up to the leads was completely immersed in it. The condenser satisfied the conditions as laid down by Hartshorn and Oliver.[2d] The rigidity of the test condenser-plates and the constancy of its value were put to test by a number of preliminary experiments which showed that the condenser could be used reliably for quantitative work.

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[4] Normann, *Chem. Z.*, 1907, 3, II.

[5] Baker, *Chem. Weekblad.*, 1915, 1034.

[6] Held, *Inaug. Dissert.*, 1909, Libertwolkwitz.

[7] Constructed according to F. M. Colebrock, *Wireless World*, 1931, **29**.

[8] Moullin, *Wireless World*, 1922, **10**, 1; *J. Inst. Elec. Eng.*, 1923, **61**, 295; Austin, *Phys. Rev.*, 1929, **34**, 300.

Discussion.

Table III gives the net results of these experiments. In Fig. 2 curves are drawn by plotting the dielectric constant (E) of the solution against the

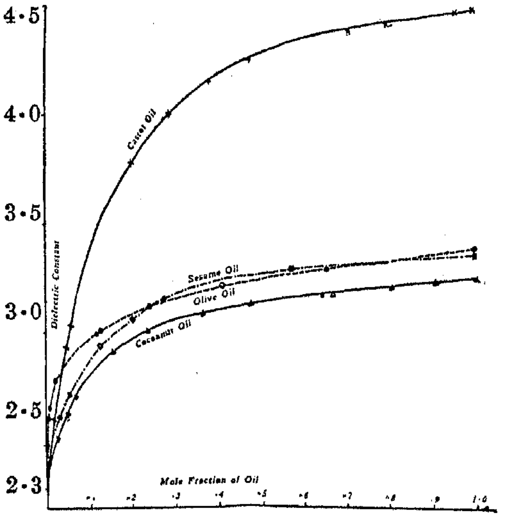


FIG. 2. Dielectric constant against mole fraction of oil.

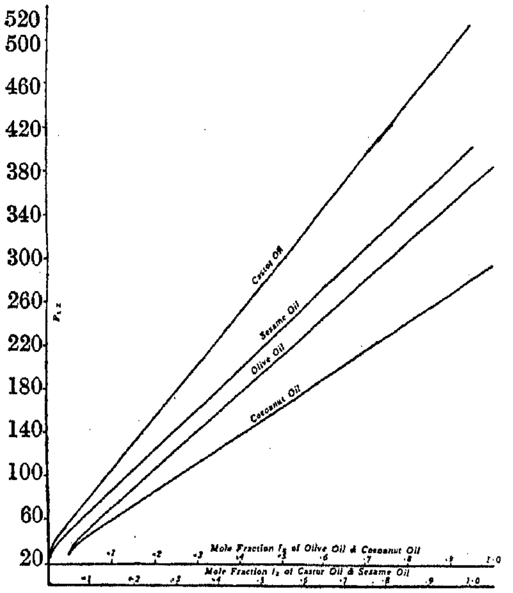


FIG. 3. Molar Polarization $P_{1,2}$ of Solution of Oil in Benzene against Mole Fraction f_2 of Oil.

TABLE III.

	Castor Oil	Olive Oil	Sesame Oil	Cocoanut Oil
Molecular weight	935	830	848	638
Density	0·9612	0·9125	0·9132	0·9204
Dielectric constant	4·478	3·352	3·365	3·254
Refractive Index	1·4745	1·4665	1·4675	1·4521
Molar polarization P_2	521·7	399·6	409·3	297·4
Molar polarization at infinite dilution P_∞	554	437	434	352
Electronic polarization P_E ..	273·6	246·8	258	187
Orientation polarization P_O ..	280·4	190·2	176	165
Electric Moment $\times 10^{\pm 18}$ ..	3·68	3·03	2·91	2·82

mole fraction (f_2) of the oil. They all show a similar nature of variation with concentration with a steep initial rise up to 0·1 to 0·2 mol. fraction, and then a flat course. This may be attributed to the association of the oil molecules. Curves in Fig. 3 show the variation of the molecular polarization ($P_{1,2}$) of the solution with the mole fraction of the oil. $P_{1,2}$ was calculated by the equation:

$$P_{1,2} = \frac{E-1}{E+2} \cdot \frac{M_1 f_1 + M_2 f_2}{d} = P_1 f_1 + P_2 f_2.$$

In all cases $P_{1,2} - f_2$ curves have a small yet definite curvature in the dilute region though at higher concentrations they tend to be linear. The tendency of the curves to be linear at higher concentrations indicates that at these concentrations the molecules affect one another in such a way that the average field of the molecules is neutralised by the interaction resulting from the orientation of the molecules. With increasing concentration the molecules associate to form complex molecules which will have a resultant moment less than that of the individual molecule. The external field now acts not on the individual molecule having a large moment but on a complex molecule having comparatively small moment. These complex molecules, therefore, contribute little to the orientation polarization. Hence $P_{1,2} - f_2$ curves and also the $P_2 - f_2$ curves become practically linear in the region of high concentrations though the individual molecule has strong electrical moment.

A study of the change in the electronic polarization of the different oils with concentration was also undertaken with a view to determine how far

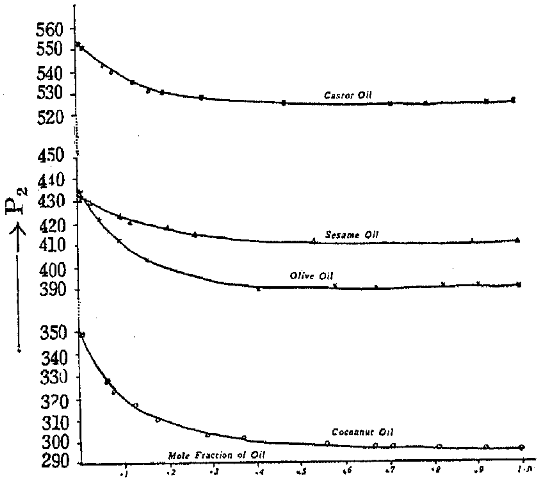


FIG. 4. Molar Polarization P_2 of oil against mole fraction f_2 of oil.

the values of the total polarization are affected by it. The values of $P_{E1,2}$ (observed) were calculated from the equation:

$$P_{E1,2} = \frac{n^2-1}{n^2+2} \cdot \frac{M_1 f_1 + M_2 f_2}{d}$$

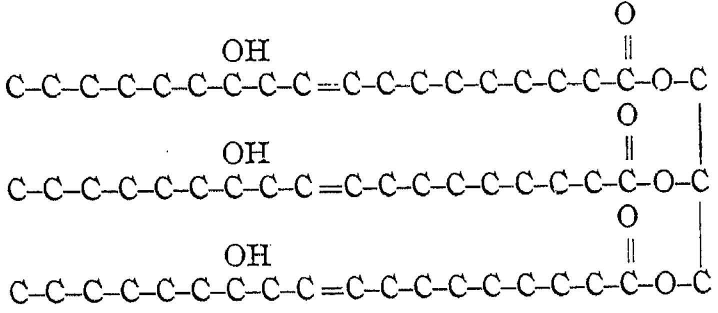
which gives the total effect, n being the refractive index determined experimentally. The values $P_{E1,2}$ (calculated) were computed from the equation:

$$P_{E1\text{-}2} = P_{E_1} f_1 + P_{E_2} f_2$$

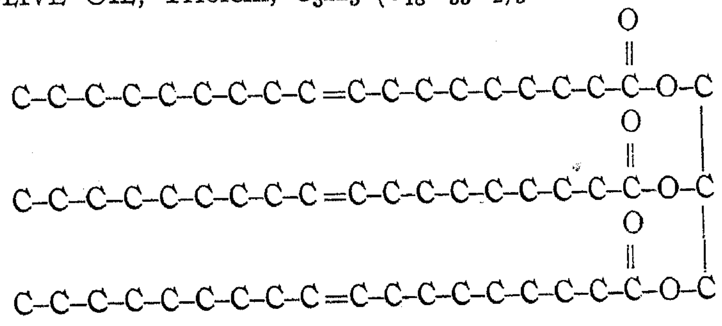
on the assumption that the total polarization follows the additive law. The difference between the two values is so small that the effect of the surrounding molecules on the electronic polarization seems to be negligible. In other words P_{E1} and P_{E2} are constant as far as can be measured through the mixture, the contribution to the polarization by the electronic shifts induced in a molecule being practically independent of the surrounding molecules.

The so-called fixed vegetable oils and fats consist chiefly of triglycerides[9] and the glyceride forming the highest percentage component of the oil may be considered as representing that oil. The structural formulæ of the chief constituents of the four oils are given below. In view of a reasonable agreement between the values of the molecular weights of the oils as determined actually and those calculated from these glycerides, it may be supposed that the assumption that these oils are represented by the respective glycerides is not without any foundation. The formula for the glycerides can be written, as Stoops has done, thus:

CASTOR OIL, Triricinolein, $C_3H_5\ (C_{18}H_{33}O_3)_3$.



OLIVE OIL, Triolein, $C_3H_5\ (C_{18}H_{33}O_2)_3$.



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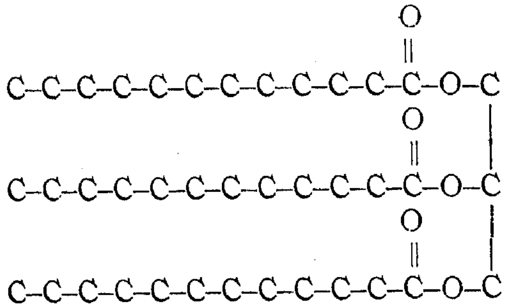
[9] Thorpe, *Dictionary of Applied Chemistry*, 4, 645.

SESAME OIL, Triolein, $C_3H_5\ (C_{18}H_{33}O_2)_3$.

Same as for Olive Oil.

COCOANUT OIL, Trilaurin, $C_3H_5\ (C_{12}H_{23}O_2)_3$.



The hydrogen atoms are omitted in these formulæ.

These formulæ can sufficiently account for the observed differences in moment. The value for cocoanut oil containing mostly trilaurin is in fair agreement with the value $2 \cdot 7 \times 10^{-18}$ found by Stoops for pure Tristearin. A double bond in each of the side chains of triolein apparently causes the slight rise in moment of olive and sesame oils, and the further presence of the three strongly polar OH groups in triricinolein of castor oil brings about the sharp rise in moment of the latter to $3 \cdot 7 \times 10^{-18}$.

The oils studied here give a fairly complete range, castor oil containing hydroxyl and hydroxy esters, olive oil and sesame oil the unsaturated ones and the cocoanut oil completely saturated ester. The values for the electric moments of these oil molecules therefore support the statement of Stoops that reasonably moments of vegetable oils and fats (also animal oils and fats) should have values in the range $2 \cdot 7$ to $3 \cdot 7$ depending on the constitution of the acids of which they are composed.

Summary.

The density, the refractive index and the dielectric constants at room temperature (26°) are determined for the solutions of castor oil, olive oil, sesame oil and cocoanut oil in benzene. The dielectric constants were determined at 30 meters (10,000 Kc.) by observing the resonance with the help of a valve-voltmeter. It is found that in very dilute solutions the molecules of these oils are more or less free from association. Experiments on very dilute solutions of these oils therefore give fairly reasonable values for their electric moments which are in these cases $3 \cdot 68 \times 10^{-18}$; $3 \cdot 03 \times 10^{-18}$; $2 \cdot 91 \times 10^{-18}$; and $2 \cdot 82 \times 10^{-18}$ for castor oil, olive oil, sesame oil and cocoanut oil respectively.