The Specific Refraction of Fatty Oils

M. TELS, A. J. KRUIDENIER, C. BOELHOUWER, and H. I. WATERMAN,
Technological University, Delft, The Netherlands

MANY RELATIONSHIPS between various physical and chemical constants of fatty oils have been published. Most of these are completely empirical, such as, for instance, the well known equations given by Lund (9) in 1922.

Other authors obtained correlations between the constants by applying to fatty oils the principle of additivity of Lorenz-Lorentz atomic and group refractions. In 1934 Waterman (19) published a diagram correlating the specific refraction and the I.V.[1] of mixtures of triglycerides with 57 carbon atoms per molecule (tristearin, triolein, etc.). This diagram has been instrumental in clarifying the reaction mechanism of the SO_2-catalyzed polymerization of linseed oil. In 1916 Backer (1) derived a relationship between the specific refraction, the I.V. and the S.V. of fatty oils. Both Backer and Waterman however used the values of the atomic and group refractions calculated by Roth and Eisenlohr (5). These values are now known to be inaccurate. The deviations of the specific refractions calculated by these authors from those determined experimentally are therefore large (1, 20). Backer solved this difficulty by introducing an empirical correction into the constant term of his equation. Consequently his corrected equation lacks a fundamental basis though it does not differ much from the equation derived in the present paper.

In 1954 Hammond and Lundberg (8) published a system of correlations between the molar volumes, the molar refractions, and the refractive indices of pure fatty acid esters of monovalent alcohols, fatty acids, and other fatty acid derivatives. These authors applied the principle of additivity of atomic and group refractions to the pure compounds they studied. Hammond and Lundberg considered the data at present available to be inadequate for calculating the refractions of triglycerides or mixtures of triglycerides. This opinion is undoubtedly correct if no atomic and group refractions are used other than those obtained from determinations of the constants of triglycerides.

The refractions of the methylene group and the hydrogen atom are known with a high degree of accuracy from many determinations of the refractive indices, the densities, and the molecular weights of a large number of pure hydrocarbons and mixtures of hydrocarbons (2, 6, 11, 12, 14, 16). If these refractions are used in calculating the specific refractions of triglycerides, a graphical statistical diagram, covering the whole field of all theoretically possible mixtures of triglycerides of nonpolymerized, nonconjugated, straight-chain fatty acids, can be developed.

Group Refraction of the Methylene Group in Methyl Esters of Saturated Fatty Acids

The general formula of methyl esters of saturated fatty acids can be represented as

$$C_{n_c}\, H_{2n_c}\, O_2$$

when n_c is the number of carbon atoms in the ester molecule.

If

$R_M = \left[\frac{n^2-1}{n^2+2}\right]\frac{M}{d} =$ molar refraction of the ester,
$R_{CH_2} =$ group refraction of the methylene group,
$R_{=O} =$ atomic refraction of the carbonylic O-atom
$R_{-O-} =$ atomic refraction of the etheric O-atom,
$r = R_M/M =$ specific refraction of the ester,
$M =$ molecular weight of the ester,
$d = d_4^{20} =$ density of the ester,
$n = n_D^{20} =$ refractive index of the ester,

it follows from the principle of additivity of atomic and group refractions that

$$r = R_M/M = \frac{1}{M}\left(n_c R_{CH_2} + R_{=O} + R_{-O-}\right) \qquad (1)$$

where $M = (12.010 + 2.016)\, n_c + 32 \qquad (2)$

By eliminating n_c from equations *(1)* and *(2)*, it follows that

$$r = \frac{R_{CH_2}}{14.03} + \frac{R_{=O} + R_{-O-} - \frac{32}{14.03}R_{CH_2}}{M} \qquad (3)$$

Schenk, Vervoorn, Waterman, and Weber (14) have shown that R_{CH_2} is not completely independent of M, but the variation of R_{CH_2} is so small as to be negligible in this case. Equation *(3)* may therefore be written as

$$r = A + B/M \qquad (4)$$

where A and B are constants while

$$A = R_{CH_2}/14.03 \qquad (5)$$

A and B are found by substitution of the known values of r and M of six methyl esters into equation *(4)*. The best values for A and B, determined by trial and error, are

$$A = 0.3309 \qquad B = -6.99$$

In Table I the values of r, as calculated from equation *(4)* with the above values of A and B, are compared with the experimental values of the six esters. The experimental values of Table I and Table V were taken from the paper by Hammond and Lundberg (8).

TABLE I

Comparison of Observed and Calculated Values for r_D^{20} in Methyl Esters

Methyl ester	M	R_M Observed	r_D^{20} Observed	r_D^{20} Calculated	Deviation
Propionate	88.10	22.17	0.2516	0.2516	0.0000
Caproate	130.18	36.09	0.2772	0.2772	0.0000
Caprylate	158.23	45.35	0.2866	0.2867	+0.0001
Caprate	186.29	54.63	0.2933	0.2934	+0.0001
Laurate	214.34	63.91	0.2982	0.2983	+0.0001
Myristate	242.39	73.24	0.3022	0.3021	−0.0001

---

[1] I.V. = iodine value; S.V. = saponification value.

The value of R_{CH_2} in methyl esters of saturated acids can be calculated from equation *(5)*:

$$R_{CH_2} = 14.03 \times A = 4.643$$

In Table II this value is compared with the values obtained by other authors from other series of compounds.

TABLE II

Comparison of Values of R_{CH_2} (various authors)

Author	R_{CH_2}		Year Reference	
Eisenlohr	4.618	various compounds	1911	5
Merckx	4.636	nitriles	1933	10
Wibaut, Langedijk	4.638	alkanes	1940	21
Geldof, Wibaut	4.637	*n*-alkenes	1948	7
Smittenberg	4.640	*n*-alkanes and other series	1948	11
Schuhmacher	4.639	branched alkenes	1953	16
Vogel	4.647	alkyl halogenides,alkanes	1955	18
de Booijs	4.640	pure hydrocarbons	1955	2
Schenk, c.s.	4.642	pure hydrocarbons	1956	14
Geelen	4.643	mixtures of saturated hydrocarbons	1956	6
This article	4.643	methyl esters of satur. fatty acids	1957	...

It is clear that the value of R_{CH_2} found here is in very good agreement with the modern values obtained by several authors (mostly from the physical constants of hydrocarbons). We may therefore assume the value of R_{CH_2} in fatty acid esters to be equal to the same value in hydrocarbons.

The values of R_{CH_2}, as given in Table II, were in all cases obtained from a large number of more reliable data than are at present available in the field of fatty acid esters. For this reason the authors prefer, in these fatty acid ester calculations, using a value of R_{CH_2} obtained from hydrocarbons rather than relying on the value derived from the data on the mere six methyl esters mentioned above.

The value chosen is that given by Smittenberg (11) and also by de Booijs (2):

$$R_{CH_2} = 4.640 \qquad (6)$$

By substituting this value into equation *(3)*, it is found that

$$R_{=O} + R_{-O-} = R_M - 0.3307\,M + 10.583 \qquad (7)$$

The values of $R_{=O} + R_{-O-}$, calculated from equation *(7)* and the physical constants of the saturated methyl esters, are given in Table III.

TABLE III

Values of $R_{=O} + R_{-O-}$ Calculated from Constants of Methyl Esters of Saturated Fatty Acids

Methyl ester	$R_{=O} + R_{-O-}$
Propionate	3.62
Caproate	3.62
Caprylate	3.60
Caprate	3.61
Laurate	3.61
Myristate	3.66

As follows from Table III, the mean value of $R_{=O} + R_{-O-}$ amounts to 3.62; and the largest deviation, 0.04, can only have a small influence on the value of r.

The Influence of the Double Bond

If a double bond is introduced into a compound M, whereby a nonconjugated, unsaturated compound N is formed, the difference between the molar refractions R_M and R_N is equal to the difference between the group refractions of the groups

$$-CH_2-CH_2- \quad \text{and} \quad -CH=CH-$$

This difference is equal to

$$R_M - R_N = 2\,R_H - I = I_{DH} \qquad (8)$$

where I is the increment of the double bond. The value of I_{DH} calculated from the physical constants of hydrocarbons is again assumed to be equal to the same value in fatty acid esters. Values of I_{DH}, calculated from constants determined by Rossini (12), are given in Table IV.

TABLE IV

Values of $I_{DH} = R_{alkane} - R_{alkene}$ for a Number of Straight-Chain Hydrocarbons

Alkane	Alkene	R_{alkane}	R_{alkene}	I_{DH}
Pentane	pentene-1	25.266	24.854	0.412
Pentane	*cis*-pentene-2	25.266	24.95	0.32
Hexane	hexene-1	29.907	29.492	0.415
Hexane	*cis*-hexene-2	29.907	29.55	0.36
Hexane	*cis*-hexene-3	29.907	29.67	0.24
Heptane	heptene-1	34.550	34.135	0.415
Heptane	*cis*-heptene-2	34.550	34.0	0.6
Heptane	*cis*-heptene-3	34.550	34.30	0.25
Octane	octene-1	39.192	38.778	0.414
Octane	*cis*-octene-2	39.192	38.79	0.40
Octane	*cis*-octene-3	39.192	38.8	0.4
Octane	*cis*-octene-4	39.192	38.95	0.24
Pentane	*trans*-pentene-2	25.266	25.02	0.25
Hexane	*trans*-hexene-2	29.907	29.64	0.27
Hexane	*trans*-hexene-3	29.907	29.75	0.16
Heptane	*trans*-heptene-2	34.550	34.28	0.27
Heptane	*trans*-heptene-3	34.550	34.42	0.13
Octane	*trans*-octene-2	39.192	38.88	0.31
Octane	*trans*-octene-3	39.192	39.09	0.10
Octane	*trans*-octene-4	39.192	39.08	0.11

It follows from Table IV that I_{DH} is not only dependent on the steric configuration around the double bond but also on the position of the double bond in the carbon chain. At the moment it is necessary to choose one single value for I_{DH} in all the calculations. This obviously gives rise to inaccuracies in the results of some of the calculations: isomers like methyl oleate and methyl petroselenate cannot and, in fact, do not have the same specific refractions.

The value for I_{DH} was chosen on the following grounds. It is generally assumed that most double bonds in natural fatty oils have a *cis*-configuration. The position of the double bonds in many fatty acids is more or less in the middle of the carbon chain. From a comparison of the values of I_{DH} in *cis*-hexene-3, *cis*-heptene-3, and *cis*-octene-4 (compare Table IV) it follows that

$$I_{DH} = 0.24 \qquad (9)$$

is a reasonable value.

Data on nonconjugated polyenes with a carbon chain of sufficient length are not at present available. Hammond and Lundberg (8) however observed that the use of one single value of I_{DH} for both polyenes and monoenes seems to be justified. This observation is confirmed by the present calculations. The specific refraction of a methyl ester of a fatty acid containing n_c carbon atoms and q double bonds is equal to

$$r = \frac{1}{M}\left(n_c R_{CH_2} + R_{=O} + R_{-O-} - q\,I_{DH}\right) \qquad (10)$$

A comparison between the calculated and observed specific refractions of some unsaturated methyl esters is given in Table V.

TABLE V

Comparison Between Calculated and Observed Specific *Refractions of Unsaturated Methyl Esters*

Methyl ester	r_D^{20} Observed	r_D^{20} Calculated	Deviation
Oleate	0.3087	0.3088	+0.0001
Oleate	0.3090	0.3088	—0.0002
Petroselenate	0.3067	0.3088	+0.0021
Erucate	0.3123	0.3123	0.0000
Arachidonate	0.3135	0.3143	+0.0008

Triglycerides and Mixtures of Triglycerides

The formula of a saturated triglyceride is

$$(CH_2)_{n_c} H_{-4} O_6,$$

the specific refraction is equal to

$$r = \frac{1}{\overline{M}} \left[n_c R_{CH_2} + 3 \, (R_{=O} + R_{-O-}) - 4R_H \right] \quad (11)$$

The value of R_H is again assumed to be equal to the same value obtained from the physical constants of hydrocarbons. The mean value of R_H in hydrocarbons, calculated by de Booijs (2) from constants determined by Rossini (12), is chosen:

$$R_H = 1.043 \quad (12)$$

A comparison between the specific refractions of some symmetric triglycerides obtained from constants determined by Scheij (15), and the specific refractions of these compounds calculated from equation *(11)* is given in Table VI. Where the constants were not determined at 20°C., the following temperature coefficient of the specific refraction is used:

$$dr/dt = 0.00002 \quad (13)$$

This relation holds between 15°C. and 80°C. (1).

Data in Table VI show that the deviations are of the second order of magnitude over a rather wide range of values of the specific refraction.

TABLE VI

Comparison Between Calculated and Observed Values for r_D^{20} of Pure Triglycerides

Triglyceride	r_D^{20} Observed	r_D^{20} Calculated	Deviation
Tributyrin	0.2532	0.2523	—0.0009
Tricaproin	0.2685	0.2694	+0.0009
Tricaprylin	0.2807	0.2804	—0.0003
Tricaprin	0.2885	0.2880	—0.0005
Trilaurin	0.2941	0.2937	—0.0004
Trimyristin	0.2987	0.2980	—0.0007
Tripalmitin	0.3021	0.3014	—0.0007
Tristearin	0.3044	0.3042	—0.0002

It is now assumed that all atomic and group refractions calculated above are additive in mixtures of triglycerides containing nonconjugated, nonpolymerized, straight-chain fatty acids.

The symbols to be used in calculations on mixtures are:

$\overline{n}_c$ = mean number of carbon atoms per molecule
$\overline{q}$ = mean number of double bonds per molecule
$\overline{M}$ = mean molecular weight

If the above assumption is valid, it follows that

$$R_{mixture} = \overline{n}_c R_{CH_2} + 3(R_{=O} + R_{-O-}) - 4 R_H - \overline{q} I_{DH}$$

and

$$r = R_{mixture}/\overline{M} = 1/\overline{M} \quad (14)$$
$$[\overline{n}_c R_{CH_2} + 3 (R_{=O} + R_{-O-}) - 4 R_H - \overline{q} I_{DH}]$$

$\overline{n}_c$, $\overline{q}$ and $\overline{M}$ can be expressed in the more conventional I.V. and S.V.

The use of the I.V. and S.V. implies no specific method of analysis. The I.V. meant here is any measure of the degree of unsaturation of a fatty oil, provided *that it is expressed as the weight percentage of* iodine absorbed by the oil. Likewise the S.V. is any measure of the mean molecular weight of a fatty oil, provided that it is expressed as the number of milligrams of KOH required to saponify one gram of the oil.

The relationship between $\overline{M}$ and S.V. is well known:

$$\overline{M} \times S.V. = 168300 \quad (15)$$

$\overline{M}$ grams of a fatty oil absorb $\overline{M} \times$ I.V. $\times$ 0.01 grams of iodine. If the fatty oil has a mean number of $\overline{q}$ double bonds per molecule, it follows that

$$2 \times 126.92 \times \overline{q} = 0.01 \, \overline{M} \times I.V.$$

or, substituting equation *(15)* in this relationship,

$$\overline{q} \times S.V. = 6.630 \, I.V. \quad (16)$$

The average formula of a fatty oil having a mean number of carbon atoms per molecule equal to $\overline{n}_c$ and a mean number of double bonds per molecule equal to $\overline{q}$ is

$$(CH_2)_{\overline{n}_c} H_{(-2\overline{q}-4)} O_6$$

Thus $\overline{M} = 14.03 \, \overline{n}_c - 1.008 \, (2 \, \overline{q} + 4) + 96$ or, substituting equations *(15)* and *(16)* into this relationship,

$$n_c = \frac{1}{14.03} \quad (17)$$
$$\left[\frac{168300}{S.V.} + 1.008 \, (2 \times 6.630 \times \frac{I.V.}{S.V.} + 4) - 96 \right]$$

By substitution of equations *(6, 9, 12, 15, 16,* and *17)* into equation *(14)* a relationship between r_D^{20}, I.V. and S.V. is found:

$$r_D^{20} = \left[\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \right]_D^{20}$$
$$= 0.3307 + 1.68 \times 10^{-5} \, I.V. - 1.41 \times 10^{-4} \, S.V. \quad (18)$$

A comparison between the specific refractions observed by some authors and those calculated from this relationship is given in Table VII. Where the

TABLE VII

Comparison Between Observed and Calculated Specific Refractions of Some Fatty Oils

Oil	S.V.	I.V.	r_D^{20} Observed	r_D^{20} Calculated	Deviation
Peanut	191.3	83.7	0.3054	0.3051	—0.0003
Peanut hardened	190.0	5.8	0.3042	0.3040	—0.0002
Coconut	261.5	7.0	0.2950	0.2939	—0.0011
Coconut hardened	260.5	0.2	0.2950	0.2940	—0.0010
Linseed (ref. 4)	195.4	169.0	0.3056	0.3060	+0.0004
Linseed	192.0	181.3	0.3067	0.3067	0.0000
Linseed hardened	190.0	18.1	0.3043	0.3042	—0.0001
Corn	192.8	124.5	0.3052	0.3056	+0.0004
Corn hardened	191.0	23.2	0.3041	0.3042	+0.0001
Olive	192.3	83.6	0.3054	0.3050	—0.0004
Olive hardened	191.0	21.8	0.3048	0.3041	—0.0007
Olive (ref. 17)	190	85	0.3051	0.3053	+0.0002
Palm kernel	249.2	15.9	0.2966	0.2958	—0.0008
Palm kernel hardened	248.1	0.2	0.2966	0.2957	—0.0009
Rapeseed	175.2	103.2	0.3077	0.3077	0.0000
Rapeseed hardened	173.8	30.8	0.3069	0.3067	—0.0002
Sesame	191.2	108.7	0.3051	0.3056	+0.0005
Sesame hardened	191.0	69.3	0.3047	0.3049	+0.0002
Sesame hardened	190.8	48.9	0.3046	0.3046	0.0000
Sesame hardened	190.8	40.3	0.3045	0.3045	0.0000
Sesame hardened	190.8	21.2	0.3043	0.3042	—0.0001
Sesame hardened	190.8	1.0	0.3041	0.3038	—0.0003
Sesame (ref. 3)	194	115	0.3049	0.3053	+0.0004
Lard	199.0	52.8	0.3045	0.3035	—0.0010
Lard hardened	197.5	0.0	0.3036	0.3029	—0.0007
Soybean (ref. 13)	192	126	0.3054	0.3057	+0.0003

constants were not determined at 20°C., equation *(13)* has been used. When no mention to the contrary is made the observed values have been taken from the paper by Backer (1).

Graphical Statistical Diagram

Figure 1 is a diagram, calculated from equations *(15, 16, 17,* and *18),* in which r_D^{20} is plotted against the I.V. The diagram is valid for triglycerides and mixtures of triglycerides of nonconjugated, nonpolymerized, straight-chain fatty acids. A point in the diagram represents an infinitely large number of mixtures of triglycerides and in some cases one pure triglyceride, having the same I.V. and S.V. The diagram can be expanded to cover the whole field of theoretically possible fatty oils.

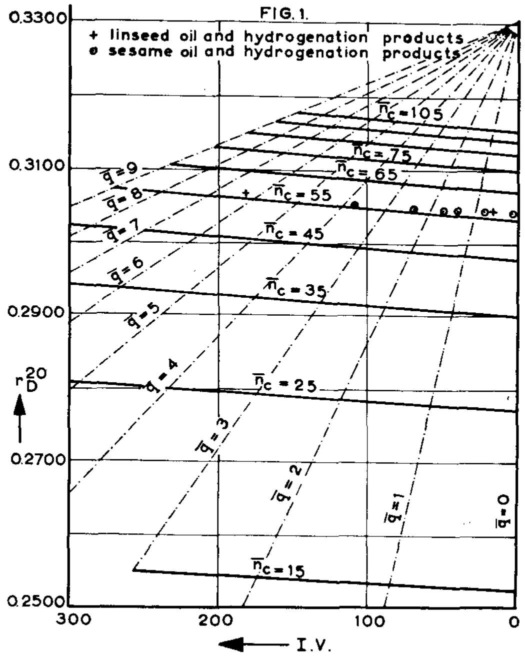

FIG. 1. Diagram for the graphical-statistical analysis of triglycerides.

Lines of equal mean number of double bonds per molecule (q) have been plotted. By substituting equation *(16)* into equation *(18),* it is found that

$$r_D^{20} = 0.3307 - (9.348 \times 10^{-4}/\bar{q} - 1.68 \times 10^{-5})\ \text{I.V.} \quad (19)$$

so the lines of equal $\bar{q}$ are straight and converge to the point ($r_D^{20} = 0.3307$; I.V. $= 0$) when $\overline{M}$ approaches infinity.

Furthermore lines of equal mean number of carbon atoms per molecule ($\bar{n}_c$) have been plotted. As it is not possible to introduce more than a certain number of nonconjugated double bonds into a triglyceride with a given number of carbon atoms per molecule, a line of equal $\bar{n}_c$ will always end at the point of intersection with a line of equal $\bar{q}$ (the line $\bar{n}_c = 15$, for instance, ends at the point of intersection with the line $\bar{q} = 3$).

The diagram and equations *(15* to *18)* serve to characterize fatty oils. If the oils are not polymerized and do not contain conjugated or branched fatty acid groups, $\bar{n}_c$, $\bar{q}$, $\overline{M}$, and r_D^{20} can be determined from the I.V. and the S.V. If r_D^{20} is also determined, the diagram and the equations can serve to indicate the presence of polymerization or conjugation (19).

If a fatty oil is hardened, $\bar{n}_c$ obviously will not change during hydrogenation. If no *cis-trans* isomerization occurs, the points in the diagram representing a fatty oil and its hydrogenation products must lie on a curve of equal $\bar{n}_c$. If *cis-trans* isomerization does occur during hardening, the deviations from this curve cannot be large, as may be seen from Table IV. The specific refractions of the hardening products of a fatty oil can therefore be indicated in the diagram.

This is shown in Figure 1 for the hydrogenation products of linseed oil and sesame oil. It will be noticed that only second order deviations from the curves of equal $\bar{n}_c$ occur during the hydrogenations. Investigations into the graphical-statistical analysis of fatty oils are continuing in this laboratory.

Summary

It is shown that atomic and group refractions, obtained from data on hydrocarbons, may be used in calculating the Lorenz-Lorentz molar refraction of fatty acid esters.

By assuming that the various atomic and group refractions are additive in mixtures of fatty acid esters, a relation between the iodine value, the saponification value, and the specific refraction of fatty oils is derived. The validity of this relation is confirmed by comparing the calculated and the experimentally determined specific refractions of a number of fatty oils and their hydrogenation products.

From this relation a diagram for the graphical-statistical analysis of glycerides of nonconjugated, nonpolymerized, straight-chain fatty acids is developed.

REFERENCES

1. Backer, H. J., Chem. Weekblad, *13,* 954 (1916).
2. de Booijs, C. L., thesis 1955, Technological University, Delft, The Netherlands.
3. Dahmen, E. A. M. F., thesis 1946, Technological University, Delft, The Netherlands.
4. Van Dam, J., unpublished results.
5. Eisenlohr, F., "Spektrochemie Organischer Verbindungen," 1st ed., p. 48, Stuttgart, Verlag von Ferdinand Enke, 1912; Roth, W. A., Eisenlohr, F., and Löwe, F., "Refraktometrisches Hilfsbuch," 2nd. ed., p. 135, Berlin, N. de Gruyter and Co., 1952.
6. Geelen, H., thesis 1956, Technological University, Delft, The Netherlands.
7. Geldof, H., and Wibaut, J. P., Rec. trav. chim., *67,* 105 (1948).
8. Hammond, E. G., and Lundberg, W. O., J. Am. Oil Chemists' Soc., *31,* 427 (1954).
9. Lund, J., Z. Untersuch. Nahr. Genussm., *44,* 113 (1922).
10. Merckx, R., Verhulst, J., and Bruylants, P., Bull. soc. chim. Belges, *42,* 177 (1933).
11. Van Nes, K., and Van Westen, H. A., "Aspects of the Constitution of Mineral Oils," 1st ed., Amsterdam, Elsevier Publishing Company Inc.
12. Rossini, F. D., "Selected Values of Physical Constants and Thermodynamic Properties of Hydrocarbons and Related Compounds," A.P.I. Research Project 44.
13. de Ruiter, J. J., unpublished results.
14. Schenk, P., Vervoorn, A. B. H., Waterman, H. I., and Weber, A. B. R., J. Inst. Petrol., *42,* 205 (1956).
15. Scheij, L. T. C., Rec. trav. chim., *18,* 169 (1899).
16. Schuhmacher, J. P., thesis, Municipal University of Amsterdam, 1953, Amsterdam, The Netherlands.
17. Van Vlodrop, C., thesis, 1938, Technological University, Delft, The Netherlands.
18. Vogel, A. I., "Practical Organic Chemistry," 3rd ed., p. 1035, London, Longmans, Green and Company, 1955.
19. Waterman, H. I., Compt. rend. XIV congr. chim. ind., Paris, 1934.
20. Waterman, H. I., and Van Vlodrop, C., Compt. rend. XV congr. chim. ind., Brussels, 1935, p. LXXXV.
21. Wibaut, J. P., and Langedijk, S. L., Rec. trav. chim., *59,* 1220 (1940).

[Received July 9, 1957]