function of the specific gravity of the liquid used. In the control sample the solids phase amounted to 50.4% whereas, at specific gravity 0.9344, a minimum weight of solids phase of 38.8% was attained. This spread contained 18% by weight of monoglyceride; thus the ratio of solids-phase residue to solids added to the spread was 2.15. The difference in amount of solids added and amount of solids phase found after centrifugation probably arose from oil so entrapped as not to be released in the centrifugation rather than from solids removed from the oil by means of solubility in the monoglycerides. Hence this procedure offers promise only of an enrichment of the solids rather than a complete separation.

Summary

By means of the analytical ultracentrifuge the rate of separation of a plastic spread into liquid and solids phases was observed and the proportions of each phase determined. An estimate of the amount of true solids was complicated by the fact that the solids phase consisted of approximately one-half oil.

In the preparative ultracentrifuge sufficient quantities of the oil phase were isolated for chemical analysis. Centrifugation at each of several temperatures and analysis of the oil and solids phases would yield a characterization of the different components which crystallize at various temperatures.

By centrifuging the plastic spread with a layer of aqueous alcohol of density intermediate to the oil and solids, the solids phase was separated more nearly oil-free. The solids phase however still was not sufficiently pure to permit a chemical characterization representative of the solid component. Corrections can be made however for the effect of occluded oil.

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REFERENCES

1. Bailey, A. E., "Melting and Solidification of Fats," p. 310, New York, Interscience Publishers Inc., 1950.
2. Fulton, N. D., Lutton, E. S., and Wille, R. L., J. Am. Oil Chemists' Soc., *31*, 98-103 (1954).
3. Jones, E. P., Dutton, H. J., and Cowan, J. D., J. Am. Oil Chemists' Soc., *30*, 609-610 (1953).
4. Mohr, W., and Baur-Kiel, J., Vorratspflege u. Lebensmittelforsch., *2*, 383-393 (1939).
5. Nichols, J. B., and Bailey, E. D., in "Technique of Organic Chemistry," edited by A. Weissberger, 2nd ed., vol. 1, part 1, pp. 621-731, New York, Interscience Publishers Inc., 1949.
6. Svedberg, T., and Pedersen, K. O., "The Ultracentrifuge," pp. 478, Oxford, Clarendon Press, 1940.

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A Method for the Quantitative Determination of Ethylene Oxide Adducts in Their Aqueous Solutions or Dispersions

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IN a preliminary publication (1) a method for the quantitative determination of ethylene oxide adducts has been described in their aqueous solutions or dispersions This method will now be reported in more detail.

The literature in the field is comparatively scarce. Shaffer and Critchfield (2) describe two methods, one gravimetric, the other colorimetric, for the determination of solid polyethylene glycols by precipitation with silicotungstic and phosphomolybdic acid. Haakh, v. Candié, and Möbus (3) precipitate ethylene oxide adducts by a resorcine-glucose condensation product and determine the precipitate gravimetrically. Oliver and Preston (4) precipitate the ethylene oxide compounds with phosphomolybdic acid and barium chloride in hydrochloric acid solutions, establishing a weight ratio of the complex to the precipitating agent used. Coppini and Cameroni (5) describe a colorimetric, and Coppini and Grassi (6) an iodometric method for the determination of certain carbowax compounds. Wurzschmitt (7) reviews qualitative analytical reactions for the identification of capillary-active substances, *i.e.*, ethylene oxide products, systematically.

In the present investigations we have tried to find a method which is suitable even for factory control with stress laid upon easy handling. Due to the great versatility and variety of ethylene oxide compounds, which frequently are used together with other substances, *e.g.*, builders, it was not possible to prove the applicability in all cases but it is easily checked in every instance.

Method

The starting point of this investigation was the observation of v. Baeyer and Villiger (8) that ferrocyanic acid, H_4 $[Fe(CN)_6]$ gives addition products with diethyl eter. Several modifications led to the following method:

Reagents

1. 0.25 M potassium ferrocyanide, reagent grade containing 0.5 g. anhydrous sodium carbonate per liter.
2. Ammonium sulfate-solution containing 400 g. recrystallized $(NH_4)_2SO_4$ per liter.
3. Sodium chloride, reagent grade.
4. Hydrochloric acid reagent grade, spec. gr. 1.18.
5. 1% diphenylamine (1 g. + 99 g. sulphuric acid, spec. gr. 1.84).
6. 2% potassium ferricyanide (2 g. + 98 ml. distilled water).
7. 0.075 M zinc sulfate reagent grade.
8. For washing of the precipitate, the following solution is used: 840 ml. distilled water, 240 g. NaCl and 80 ml. HCl spec. gr. 1.18.
9. Filter paper: J. H. Munktell's Swedish filtering paper No. 3.

Procedure

100-ml. solution containing essentially not more than 0.3 g. of the ethylene oxide adduct is placed in a 300-ml. Erlenmeyer flask, and 10 ml. of hydrochloric acid (spec. gr. 1.18) and 15 g. of sodium chloride are added. The mixture is shaken until all the salt is dissolved. Then 5.0 ml. of potassium ferrocyanide is added. The Erlenmeyer flask is shaken again, and, after standing for a few minutes, the precipitate is filtered and washed with 25 ml. of washing solution.

After washing, 5 ml. of ammonium sulfate solution, 5 drops of 2% potassium ferricyanide, and 5 drops of 1% diphenylamine are added to the filtrate, which is titrated

TABLE I

Amount of Ferrocyanic ac. (g.) Required for Precipitation

Adduct g.	un. ethyl. ox. per mole p.-octyl phen.					un. ethyl. ox. per mole oleyl alcohol			un. ethyl. ox. per mole oleyl amine		
	6.3	9.2	12.4	15.6	17.8	6.2	9.4	12.4	6.5	20.1	30.3
0.30	0.097 0.096	0.124 0.124	0.157 0.156	0.164 0.163	0.177 0.176	0.086 0.085	0.132 0.131	0.149 0.149	0.115 0.111	0.171 0.169	0.192 0.191
0.24	0.082 0.080	0.102 0.102	0.128 0.126	0.135 0.136	0.144 0.144	0.079 0.081	0.108 0.107	0.120 0.120	0.101 0.102	0.142 0.143	0.156 0.157
0.12	0.039 0.040	0.054 0.054	0.068 0.067	0.070 0.069	0.073 0.072	0.039 0.040	0.055 0.054	0.059 0.059	0.054 0.050	0.074 0.072	0.077 0.075
0.06	0.019 0.020	0.027 0.029	0.036 0.034	0.037 0.037	0.038 0.035	0.018 0.019	0.026 0.026	0.031 0.031	0.022 0.024	0.037 0.037	0.041 0.043
0.03	0.012 0.011	0.015 0.015	0.016 0.018	0.017 0.017	0.017 0.017	0.008 0.008	0.013 0.013	0.016 0.016	0.014 0.011	0.019 0.018	0.021 0.022
1.00 m (calc.) m.d.	0.304 7.9%	0.451 3.3%	0.552 4.7%	0.573 2.6%	0.594 2.4%	0.306 7.9%	0.441 2.3%	0.507 2.5%	0.407 7.6%	0.599 2.5%	0.666 4.5%

without delay with 0.075 M zinc sulfate (9). The solution becomes greenish, and at the end-point it changes to blue-violet.

The zinc sulfate solution should be standardized against 100 ml. of blank solution. An empirical factor (f) is calculated for each ethylene oxide adduct by carrying a series of known quantities of the ethylene oxide adduct in question through the procedure. A standard curve is thereby constructed. The empirical factor (f) can be calculated from the equation of f = x/c-b where x is the amount of ethylene oxide adduct, c the initially added amount of ferrocyanic acid (determined by titration with zinc sulfate solution), and b the amount of ferrocyanic acid left in the filtrate and estimated as above. Thus c-b is the amount required for the precipitation of the ethylene oxide adduct. By knowing (f), the ethylene oxide compound content of a sample can be calculated from the standard curve.

Notes

1. The solutions of potassium ferrocyanide, diphenylamine, and potassium ferricyanide should be kept in dark bottles.
2. The potassium ferricyanide solution is discarded when more than 4 days old.
3. Some adducts may be difficult to determine because of their poor dispersibility. In some instances this can be counteracted by adding the potassium ferrocyanide solution immediately after the addition of hydrochloric acid and before the sodium chloride.
4. Titrate first with moderate haste and drop-wise near the end-point.
5. When washing a highly dispersible precipitate, the washing solution should be added cautiously in small portions.
6. It is easier to observe the end-point of the titration with daylight or a daylight lamp.
7. Do not allow the samples to stand long before titration.
8. Generally the filtration can be carried out with filter paper No. 3. However in some cases No. 00 may be preferable for obtaining a clear filtrate.

The following Table I illustrates the results obtained with the method. The first column shows the amount of ethylene oxide adducts. The other columns contain the amounts of ferrocyanic acid necessary for the precipitation of adducts with different chain length. These amounts have been calculated in the following way. Assume that the filtrate after precipitation and washing of the ethylene oxide adduct consumes m ml. of 0.075 M zinc sulfate. Furthermore let us assume that the solution containing 5.0 ml. 0.25 M ferrocyanic acid and the other additions on standardizing requires 23.0 ml. 0.075 M zinc sulfate. The theoretical value for the above-mentioned amount of ferrocyanic acid lies at 25.0 ml. of 0.075 M zinc sulfate. This gives a correction factor at 25.0/23.0. On multiplying m with this factor and subtracting from 25.0, the number of ml. zinc sulfate is obtained. This number multiplied by 0.0108 gives the corresponding amount of ferrocyanic acid in grams. It is advisable to standardize the zinc sulfate solution daily against the blank.

The adducts in Table I were prepared by condensing various amounts of ethylene oxide with commercial grade p-octyl phenol, oleyl alcohol, and oleyl amine. On examining this table, it can be noted that the reproducibility was good. The accuracy in the range 0.03 to 0.3 g. per 100 ml. is sufficient; at concentrations below 0.01 g. per 100 ml. it is less good. From the data in Table I the mean (m) and the mean deviation (m.d.) for 1.00 g. of adduct have been calculated.

From Table I the mole ratio adduct/ferrocyanic acid was calculated for p-octyl phenol + 6, 9, 12, 15, and 18 units ethylene oxide as 1 to 0.8, 1.3, 1.9, 2.3, and 2.8, respectively; for oleyl alcohol + 6, 9, and 12 units as 1 to 0.8, 1.3, and 1.8, respectively; and for oleyl amine + 6, 9, and 12 units as 1 : 0.9, 1.4, and 1.9, respectively. This ratio is the same at a constant number of ethylene oxide units.

On knowing the molecular weight of the hydrophobic part (M) and the number of ethylene oxide units in the adduct (c), it is possible to calculate from Table I the amount of ferrocyanic acid (a) required for precipitation of one g. mole of ethylene oxide:

$$a = b/c\ (M + 44c)$$

where b signifies the amount in g. of ferrocyanic acid required for the precipitation of one g. of adduct.

The following values in g. were obtained: for p-octyl phenol + 6.3, 9.2, 12.4, 15.6, and 17.8 units, 26.4, 30.4, 33.4, 33.4, and 33.4, respectively; for oleyl alcohol + 6.2, 9.4, and 12.4 units, 26.8, 32.2, and 33.2, respectively; and for oleyl amine 6.5, 20.1, and 30.3 units, 34.4, 34.4, and 35.2, respectively. As the molecular weight for ferrocyanic acid is 215.96, the mean of the values approaches to a sixth of it.

The values for (a) show, with two exceptions (some are the lowest numbers in their series), comparatively good agreement.

Conclusions

The reaction between the ethylene oxide adducts and the ferrocyanic acid takes place on the ethylene oxide chain and is independent of the hydrophobic portion of the compound. The mole ratios as well as the (a) values show for three different substances, with different hydrophobic parts, comparatively good agreement, making plausible an analogy to v. Baeyer and Villigers' observation on diethyl ether that the reaction takes place between the 0-atoms of the ethylene oxide chain and ferrocyanic acid.

The (a) values make it furthermore plausible that one mole of ferrocyanic acid is required for the precipitation of an adduct containing six units of ethylene oxide. This indicates that complete precipitation of a longer chain is easier than of a shorter one. This probably leads to an explanation as to why in Table 1 just the lowest numbers in the series show the greatest m.d. and why the above-mentioned two deviations for the (a) values were found at the lowest numbers.

Summary

A method for quantitative determination of ethylene oxide adducts is described. By precipitation in hydrochloric acid solution with a known quantity of ferrocyanic acid, filtration, and titration with zinc sulfate, the consumption of ferrocyanic acid can be determined. From the results a m.d. of less than 8% was calculated, the corresponding figure for adducts containing more than 9 ethylene oxide units does not surpass 5%. The reaction takes place on the ethylene oxide chain in the compound. To precipitate an adduct containing 6 units ethylene oxide approximately one mole of ferrocyanic acid is necessary.

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REFERENCES

1. Schönfeldt, N., Nature. *172*, 820 (1953).
2. Shaffer, C. B.. Critchfield, F. H., Ind. Eng. Chem., Anal. Edit.. *19*, 32-34 (1947).
3. Haakh, H., v. Candié, D., Möbus, W., Mell. Textil., *32*, 699-701 (1951).
4. Oliver J., Preston, C., Nature, *168*, 242 (1949).
5. Coppini, D., Cameroni, R., Boll. Chim. Farm., *92*, 363 (1953).
6. Coppini, D., Grassi, G., Atti della Soc. dei Natural. e Matemat. di Modena, 85 (1954).
7. Wurzschmitt, B., Fresenius Zeitschr. f. anal. Chem., *130*, 105-185 (1950).
8. v. Baeyer A., Villiger, V. B., *34*, 2679 (1901).
9. Galletti, M., Bull. Soc. Chim., *2*, 83 (1864).
   Kolthoff, I. M., Chemisch Weekblad, *26*, 299 (1929).

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Reactions of Fatty Materials with Oxygen. XVI.[1] Relation of Hydroperoxide and Chemical Peroxide Content to Total Oxygen Absorbed in Autoxidation of Methyl Oleate[2]

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MOST workers in this field are now in agreement that α-methylenic attack to form hydroperoxides is the major reaction in the autoxidation of monoethenoic and non-conjugated polyethenoic fatty esters. To account satisfactorily for the energetics of the reactions involved however, several investigators have proposed that in the autoxidation of monoethenoic compounds, the initial point of oxidative attack is not at the α-methylenic position but at the double bond. Only a slight amount of double bond attack is required to "trigger" the predominating α-methylenic chain reaction (1, 2, 2a, 3).

An opportunity to obtain direct experimental verification for the conclusion that hydroperoxides are the predominant initial products of autoxidation recently became available with the development of the polarographic method for determining hydroperoxides in autoxidation mixtures (12, 13). The correlation of results obtained by this method with those obtained by the chemical or iodometric method of analysis makes it possible to learn what proportion of the total peroxide content is made up of hydroperoxide, and whether in some stage of the reaction all the peroxide is present as hydroperoxide.

In a study of this type it is also essential that oxygen absorption be followed quantitatively since it is not only important to know the ratio of hydroperoxide to total peroxide but also the ratio of total peroxide to oxygen absorbed. Relatively few investigators have examined the quantitative aspects of oxygen absorption of methyl oleate (4, 8).

The use of manometric techniques offers a convenient method for measuring the amount as well as the rate of absorption of oxygen. Much of the earlier quantitative work on the autoxidation of olefins has been carried out by measuring the change in volume of oxygen at constant temperature and pressure with a gas burette. A few investigators have used the Barcroft-Warburg apparatus in which the differences in pressure as the reaction proceeds are read on a manometer while the volume and temperature are kept constant (5, 8).

For the present investigation the latter technique had real advantages. It was possible to obtain information rapidly on a large number of small samples, thereby avoiding useless waste of valuable material, yet the samples were large enough to use for the subsequent chemical and polarographic analyses.

Experimental

Materials Used. The methyl oleate (A) whose oxidation is reported in this paper was prepared from olive oil by low temperature crystallization and distillation (7), except that the free acid was crystallized three times at −55° before esterification. This material had an iodine number of 84.9, and a composition of 99.0% methyl oleate, 0.9% saturates, and 0.07% methyl linoleate (ultraviolet absorption method).

Mention will also be made of the oxidation of eight samples from a second, but slightly less pure, methyl oleate (B) (10). This ester closely approximated the first in iodine value and content of methyl oleate and saturated esters, but it had a methyl linoleate content of 0.2%.

Measurement of Oxygen Absorption. The Barcroft-Warburg apparatus and the methods used to measure oxygen absorption were similar to those described by Johnston and Frey (5) with the following exceptions. The reaction flasks contained no inner cup, mercury

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[1] Paper XV is reference 6.

[2] Presented at the Spring meeting of the American Oil Chemists' Society, San Antonio, Tex., April 11-14. 1954.

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