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A New Titrimetric Analysis for Ethylene Oxide Condensates

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NONIONIC SURFACTANTS based on ethylene oxide condensates are being used more extensively each year. Generally these condensates have hydrophobe bases of fatty alcohols, fatty acids, alkylphenols, or tall oil. They are usually tailored for a specific application, which means that not only the hydrophobe base must be specially selected but also that the amount of ethylene oxide added must be known. Likewise, in analyzing and evaluating proprietary nonionics, it is important to know the ethylene oxide content as well as the hydrophobe base.

Methods for measuring ethylene oxide content are cumbersome and time-consuming and often lack precision. Ideally the analysis should be one based on chemical methods. Morgan (4) used hydriodic acid to cleave ethylene oxide condensate ether linkages, thereby converting the polyglycol into ethyl iodide and ethylene, which were collected and determined volumetrically in standard solutions of silver nitrate and bromine, respectively.

The ester type of ethylene oxide adducts can be analyzed by saponification (1).

It was thought that hydroxyl values of the condensates could be related to ethylene oxide content when the hydrophobe base was known. An attempt to apply this method to fatty alcohol-ethylene oxide adducts of known composition was not successful however. The hydroxyl values were too high, probably because of the presence of glycols.

Other methods, both chemical and physical, for the determination of ethylene oxide content in nonionics are empirical in that they are dependent on the use of calibrations from known samples. In several methods the condensate is precipitated by heteropoly acids and, following subsequent treatment, the precipitate is titrated or analyzed colorimetrically.

A number of physical methods for ethylene oxide determination have been suggested. These methods are also based on calibration of known materials. A cloud point of aqueous solutions of nonionics *vs.* nonionic density was claimed by Steele and Berger (5) to be useful for determining the hydrophile-lipophile balance of the material and also for identifying the chemical nature of the hydrophobe. This is not applicable however to water-insoluble adducts. Greenwald *et al.* (3) titrated nonionics dissolved in dioxane and benzene with water to a turbidity end-point. The method was used to determine not only the ethylene oxide content but also the hydrophile-lipophile balance for emulsifier applications. Owing to the difficulty of purifying dioxane, the solvent was used "as received," and results were not consistent from one solvent lot to another. This and the fact that the method was not applicable to ester condensates were the main drawbacks.

Since the titration method used by Greenwald *et al.* (3) appeared to have very good precision for a given lot of dioxane, this principle was considered as a means of determining ethylene oxide content, based on calibrations of known materials. Emphasis was placed on finding a more suitable solvent since purification of dioxane to improve consistency of results is a tedious process. Of other solvents investigated, the most satisfactory was dimethylformamide (DMF).

Methods

MATERIALS

Dimethylformamide (DMF): Technical grade from du Pont was redistilled under vacuum over calcium hydride. Fraction with 51–52°C. boiling range at 19 mm. was used.

Benzene: Baker and Adamson, reagent grade.

Distilled water.

The surfactants used are described in the attached tables and figures.

EQUIPMENT

Buret: 50 ml.

Erlenmeyer flask: 125 ml.

Mohr pipette: 25 ml.

Thermometer.

PROCEDURES

1. *DMF Method*

a) A 1.00-g. sample is weighed into a 125-ml. Erlenmeyer flask.

b) Then 25 ml. of dimethylformamide plus specified weight of benzene are added to the flask.

c) The sample is dissolved by swirling and is next cooled to 20 ± 1°C. in an ice bath. Then the flask is removed from the bath.

d) Distilled water is added from a 50-ml. buret in about 2-ml. increments, and the flask is gently swirled after each addition. Since temperature rise from the heat of solution hydration is fairly high, it is necessary to insert the flask in the ice bath after each addition of water (especially at the beginning) to maintain the sample at 20 ± 1°C. A temperature of 20°C. was selected since it was easier to maintain under these conditions than a 25°C. water bath which lacked adequate cooling capacity.

The increments are decreased to 0.5 ml. when the solution on the addition of water becomes turbid before swirling. Near the endpoint, the water is added drop by drop.

e) The titration is completed when, for one minute after gently swirling the last increment

of water, typewritten print cannot be read through the turbid solution. The volume (ml.) of water used to reach this cloud end-point is recorded.

f) The volume of water found is used to prepare ethylene oxide-ml. water calibration curves. For calibration, the samples must be of known ethylene oxide content and should not differ from each other more than than 2 or 3 moles of ethylene oxide. Also the calibration should be made in duplicate. Once the calibration curve has been prepared, nonionic surfactants having the same hydrophobe base can be analyzed for ethylene oxide content.

2. *Cloud-Point Determination*
A 1.00-g. sample is dissolved in 100 ml. of water and cooled in an ice bath until the solution is clear. Then the temperature is raised slowly until the solution becomes turbid. This temperature is recorded as the cloud-point. Ethylene oxide content is read from a cloud-point *vs.* ethylene oxide content calibration curve, based on known nonionic surfactants.

3. *Ethylene Oxide by HI Cleavage*
The method used was mainly that described by Morgan (4) with partial modification to include some of Elek's (2) procedures.

Results and Discussion

DMF Method. Data presented in Table I show that there are no significant differences for titration results, using three lots of DMF to analyze three samples of fatty alcohol-ethylene oxide condensates. Use of DMF is a considerable improvement over dioxane, which gave varying results from lot to lot according to Greenwald *et al.* (3).

TABLE I
Effect of Solvent Lot on DMF Method

(25 ml. DMF + 1.25 g. Benzene at 43°C.)

Sample	Ml. of water for DMF lots		
	1	2	3
Fatty alcohol A + 4.97 EO	13.5	13.3	13.7
Fatty alcohol A + 7.59 EO	18.5	18.5	18.4
Fatty alcohol A + 9.9 EO	25.9	25.8	25.9

EO = Average moles of ethylene oxide.

Without the addition of benzene to the solvent system the end-point for all samples titrated would be too high. Use of 1.25 g. of benzene with 25 ml. of DMF for alcohol-based adducts and 1.50 g. of benzene for alkylphenol-based condensates provided optimum gradation of titration values for a wide range of ethylene oxide content.

The DMF method is dependent on solvent temperature, which changes with room temperature and also varies as heat is liberated during solvent hydration. Table II shows the effect of temperature on titration results. Since it was necessary to control temperature, 20°C. was selected as a convenient temperature to maintain. When water was added rapidly during initial titration, results were slightly higher than when added in 2-ml. increments.

After conditions for carrying out the DMF method were established, reproducibility was investigated. Table III presents data for averages of four replicate determinations and 95% confidence limits expressed in milliliters of water and moles of ethylene oxide. These data show that the test is precise to ± 0.1 mole based on calibration of knowns.

TABLE II
Effect of Temperature on DMF Method

Sample	Ml. of water at	
	20°C.	37°C.
Fatty alcohol A + 4.97 EO	10.2	13.0
Fatty alcohol A + 7.59 EO	15.3	17.5
Fatty alcohol + 9.9 EO	22.1	25.6

EO = Average moles of ethylene oxide.

TABLE III
Reproducibility of Titration by DMF Method

Sample	Avg. ml. of water for four replicates	95% CL[a]	
		Ml. H_2O	Moles EO
Fatty alcohol B + 7.5 EO	18.3	0.2	0.1
Fatty alcohol A + 8.5 EO	17.4	0.3	0.1
Octylphenol + 12.5 EO	21.0	0.1	0.1
Nonylphenol + 12.7 EO	21.9	0.1	0.1

EO = Average moles of ethylene oxide.
[a] 95% confidence limits.
Solvents:
Fatty alcohol adducts—25 ml. of DMF, 1.25 g. of benzene.
Alkylphenol adducts—25 ml. of DMF, 1.50 g. of benzene.

Calibration Curves. Figure 1 contains calibration curves giving titration values for fatty alcohol adducts. Curves for adducts of octyl-, nonyl-, dodecyl-, and dinonylphenols are presented in Figure 2. In all cases the curves are smooth and cover the ethylene oxide range normally present in nonionics based on these hydrophobes. The highest titration values given

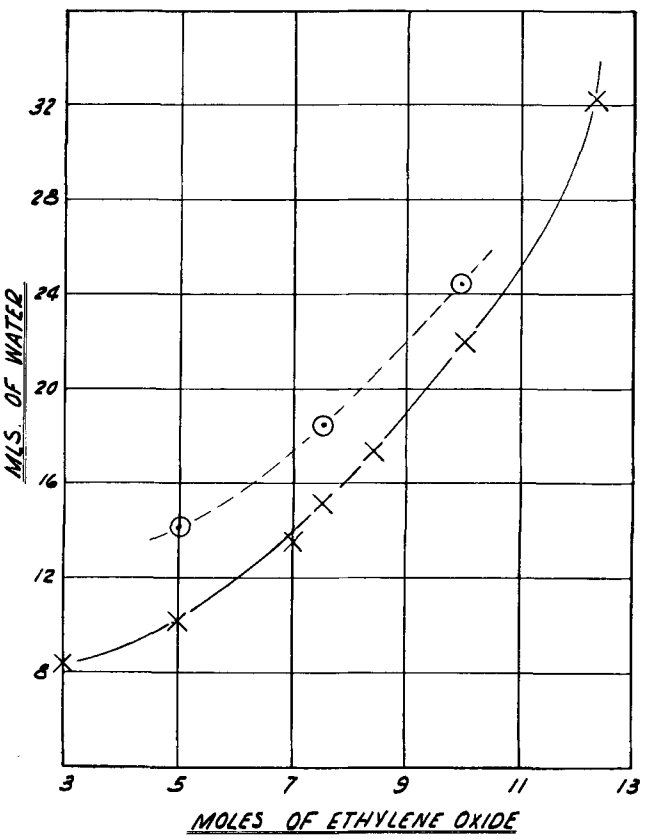

FIG. 1. Fatty alcohol adduct calibrations.
Solvent/titration:
25 ml. DMF plus 1.25 g. benzene.
×—Fatty alcohol A + ethylene oxide.
⊙—Fatty alcohol B + ethylene oxide.

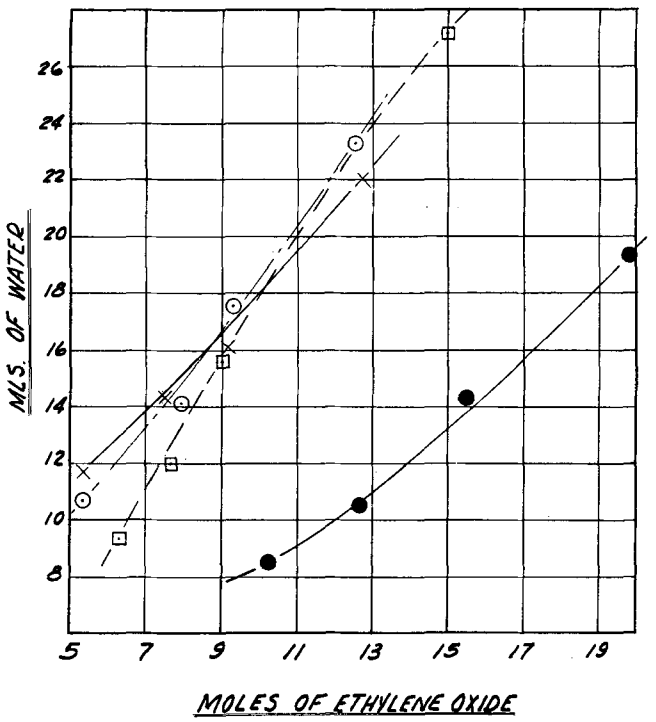

FIG. 2. Alklyphenol adduct calibrations.
Solvent/titration:
25 ml. DMF + 1.50 g. benzene.
– ——— ⊙—Octylphenol + ethylene oxide.
——— × —Nonylphenol + ethylene oxide.
— — — □—Dodecylphenol + ethylene oxide.
25 ml. DMF + 1.75 g. benzene.
——— ● —Dinonylphenol + ethylene oxide.

are for the highest ethylene oxide content suitable for titration. The ethylene oxide range can be displaced upward by use of more benzene with the DMF.

Unknown Nonionics. A group of proprietary adducts with known hydrophobes was analyzed by the DMF method. Data in Table IV list ethylene oxide content found *vs.* that known or claimed present. Titration values are in good agreement with laboratory preparation data and with reported values for proprietary products. Results are no doubt affected by the quality of hydrophobe and conditions for preparing the adduct.

Other Methods. Although the cloud-point of a nonionic surfactant solution is frequently used to determine ethylene oxide content, it has the obvious disadvantage of being applicable only to water-soluble products. Data in Table IV show that ethylene oxide by DMF and cloud-point are in fair agreement.

Unlike the methods for analysis which require reference standards of "known" ethylene oxide chain length, the HI cleavage method is absolute. The results obtained by the HI method depend solely on the sample being investigated. Theoretically the oxyethylene content of the nonionic surface-active agent is determined quantitatively by a modified alkoxyl method in which hydrogen iodide decomposes the polyglycol chain into ethyl iodide and ethylene. These compounds are collected and determined in standard solutions of alcoholic silver nitrate and bromine, respectively.

Data in Table V indicate that the method has good reproducibility. It is slightly lower than theory by about 0.1 to 0.5 moles of ethylene oxide. The HI method requires about 3 hrs. to complete while the DMF method requires less than 20 min. per analysis. The HI cleavage method should be useful as a research tool for analyzing nonionic surfactants.

TABLE IV

Ethylene Oxide Content of Unknown Nonionics

Sample	Average moles of EO by		
	Reported	Cloud-point	DMF
Fatty alcohol A + EO (lab. sample)...	5.0[a]	—[c]	5.1
Fatty alcohol A + EO (lab. sample)...	5.0[a]	—[c]	5.0
Fatty alcohol A + EO (proprietary)..	8.5[b]	8.67	8.6
Fatty alcohol A + EO (proprietary)..	8.5[b]	8.45	8.0
Fatty alcohol A + EO (proprietary)..	12.0[b]	—	11.3
Octylphenol + EO (proprietary).....	9–10[b]	—	9.0
Octylphenol + EO (proprietary).....	7–8[b]	—	7.2
Nonylphenol + EO (proprietary).....	9.5[b]	—	9.2
Nonylphenol + EO (proprietary).....	10.5[b]	—	11.5

EO = Ethylene oxide.
[a] By weight as prepared in laboratory.
[b] Value supplied by manufacturer.
[c] Cloud point < 0°C.

TABLE V

DMF Titration *vs.* Hydriodic Acid Cleavage

Sample	Average moles EO by		
	Reported	DMF	HI cleavage
Fatty alcohol A + EO.....	5.0[a]	Used to calibrate method	4.7 4.9
Fatty alcohol A + EO.....	8.5[a]	Used to calibrate method	8.3 8.4
Fatty alcohol A + EO.....	12.5[a]	Used to calibrate method	12.0, 12.2 12.1, 12.2
Nonylphenol + EO.....	9.2[a]	Used to calibrate method	8.6 8.7
Fatty alcohol A + EO.....	8.5[b]	7.7	7.1 7.2
Octylphenol + EO.....	7–8[b]	7.2	7.1 7.2

EO = Ethylene oxide.
[a] Moles EO by weight as prepared in laboratory.
[b] Moles EO reported by manufacturer.

Summary and Conclusions

A critical review of the literature was made in search of suitable methods for analyzing ethylene oxide condensates. These studies led to the development of a rapid empirical titrimetric method for measuring nonionic hydrophobicity based on a water titration of a condensate dissolved in dimethylformamide (DMF) and benzene. The end-point is identified by a definite solution turbidity. Calibration curves were prepared from known condensates.

This method should be useful for analysis of adducts in plant quality control and also for nonionics with known hydrophobes. Ether type adducts can be analyzed by this method while ester adducts cannot. (Ethylene oxide in esters can be calculated from their saponification values.) Examples of adducts which can be identified by the titrimetric method are those based on fatty alcohols and alkylphenols. Proprietary nonionics analyzed by the DMF method had ethylene oxide values in agreement with those claimed by the manufacturers. DMF data also compare favorably with that by hydriodic acid cleavage.

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Influence of Heat on Oxidative Stability and on Effectiveness of Metal-Inactivating Agents in Vegetable Oils[1]

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OUR STUDIES on lecithin as an edible oil stabilizer lead to the observation that acidic metal inactivators are not effective in undeodorized oils (4). Thus heating the oils may be necessary if an improvement in oxidative stability is to be obtained through the use of metal inactivators. The improvement in oxidative stability after heat treatments is observed in the processing of many foods. Most of the beneficial effects result from the destruction of enzymes, but heating at temperatures above those required for enzyme destruction give optimum stability.

The best example of oxidative stability resulting from heat treatments in food processing is the manufacture of dried milk (2, 6, 8, 13). Unshelled pecans (15) heated to 80°C. were found to be more stable to rancidity than the unheated controls. Walnut meats however, when blanched at 100°C., are reported to be considerably less stable to oxidation (17). Oil extracted from green coffee beans showed no improvement upon heating, but oil extracted from roasted coffee was much more stable (3). Butter showed a marked improvement upon heating to 300–400°F., but butter fat showed a decreased stability upon heating under the same condition (9). Lips (12) found that lard was not improved by heating unless certain additives, such as whey powder, were present.

The heat-imparted stability of fats is usually considered to be a direct result of peroxide destruction. We believe other factors are involved, but their elucidation is complicated. Studies on antioxidants and autoxidation are severely hampered by lack of adequate analytical methods and techniques. Baldwin (1), investigating the deodorization of corn oil, observed an optimum improvement in the stability with time of deodorization. Comparison between samples prepared by laboratory and plant deodorizations showed that temperature of about 195°C., not time, was the critical factor.

Fat peroxides are considered unstable, especially at temperatures above 100°C. Nevertheless some evaluation tests for shortening require holding the fat at 100°C. for more than 100 hrs. Other oxidative tests which depend on the development of a definite level of peroxides for the end point have used temperatures of 120° and 150°C. (11, 16). The rates of decomposition of fatty hydroperoxides have not been investigated at these higher temperatures. Our investigations on edible oils would indicate that, at a temperature of 185°C., the destruction of fatty hydroperoxides is accomplished within 30 min. Privett (20) studied destruction of hydroperoxides of lard at 100°C. under vacuum and found a 50% loss in about 14 hrs. Methyl linoleate hydroperoxide is reported to decompose at a rate of 1.6% per hour at 80°C. (7). The half-life for methyl linoleate hydroperoxide at 80°C. with an initial peroxide value of 1,222 is given as 28 hrs. (19).

[1] Presented at spring meeting, American Oil Chemists' Society, New Orleans, La., April 18–20, 1955.

Methods and Materials

Most of the oils investigated were commercially extracted, crude oils which were refined in the laboratory. A peanut oil was the only cold-pressed oil. The corn oil was hexane-extracted from wet, milled, whole corn germ in a special pilot-plant extraction, where care was taken to avoid temperatures above 95°C. during solvent stripping. The cottonseed oil was obtained as a straight, extracted crude oil, not as a mixture of prepressed and extracted oils. Commercial processors indicated that the crude oil samples had not been subjected to excessive temperatures at any time during processing. A sample of commercially refined and bleached soybean oil was also included in the study.

Oils were refined and bleached in accordance with A.O.C.S. methods. The oil samples were heated in individual, 1-liter deodorizers equipped with steam generators. Heating was done under vacuum (less 1 mm.), and agitation of the sample was accomplished by the water vapor supplied by the generator under the specified conditions of operation. No apparent change was observed in the color or condition of the oils submitted to the shorter heating times and lower temperatures. Higher temperatures and longer heating times, which approached deodorization conditions, gave the usual bleaching effect. Alcoholic solutions of the stabilizers were added to the oil after heating. In the A.O.M. stability determination the solvent was allowed to evaporate during the course of aeration. Oxidative stability data were obtained by subjecting the oil to the usual A.O.M. aeration conditions for 8 hrs. Values are reported as milliequivalents of peroxide per kilogram of oil.

Oxygen absorption studies were carried out on apparatus designed to yield samples of sufficient size (180 g.) for taste-panel evaluations. Samples were constantly shaken so that the oil was saturated with oxygen at all times; temperature was thermostatically controlled at 60°C. The oxygen absorption was calculated by the pressure drop, indicated by a manometer within the constant volume system. When stabilizer solutions were added, the solvents were removed from the oil by warming under reduced pressure before submitting the sample to an oxygen absorption test. Each 11.2 ml. of oxygen absorbed by a kilogram of fat is equal to one peroxide unit if only peroxide formation is assumed. The peroxide content of the oil and the ml. of oxygen absorbed