acids on prolonged feeding and, conceivably, could produce a *de facto* essential fatty acid deficiency. What other nutritional effects *trans* acids may have is not known. However, it is pertinent that when they are consumed as a dietary ingredient, they are found in all the common lipid classes in the tissues of the animal.

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Analysis of Detergent Mixtures Containing Amine Oxides[1]

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Abstract

Long chain alkyldimethylamine oxides in detergent mixtures have not only been difficult to determine but also interfere with anionic active analysis by the usual quaternary titration with methylene blue indicator. Titration methods have been devised for the quantitative analysis of amine oxides and anionic actives in the presence of each other and low molecular wt sulfonates. A gas chromatographic method has also been developed for determining molecular distribution in alkyldimethylamine oxide mixtures. Analytical data are presented for a series of alkyldimethylamine oxides of different mol wt and for several experimental detergent formulations. The titration method is rapid and amenable to both solid and liquid detergent formulations.

Introduction

CONSIDERABLE INTEREST has developed recently in long chain alkyldimethylamine oxides, such as dodecyldimethylamine oxide, as detergents and detergent additives. These compounds are usually made by oxidation of the corresponding amines (3), and consequently contain amines as impurities.

Several analytical methods (1,2,3,5,6,7) have been reported for amine oxides in general. However, these methods which are based either on acidimetry or reductometry are mainly for determining product purity and are not amenable to analysis of detergent mixtures. Furthermore, the presence of amine oxides in detergents interferes with the usual anionic active determination by quaternary titration with methylene blue indicator (4). Because of growing interest in these materials for detergent use, methods for determining anionic actives and amine oxides in detergents are highly desirable.

In the procedure presented, total anionic active is determined by quaternary titration of an aliquot of sample solution with bromocresol green indicator. Total amine oxide is then determined by adding a stoichiometric amount of quaternary to a second aliquot (to complex with anionic actives), extracting the mixture with chloroform, and titrating the extracted amine oxides with a standard alkylbenzenesulfonate solution and methylene blue indicator. If the mol wt of amine oxides is unknown, it can be determined by the gas chromatographic method given.

Accuracy of these methods is shown by analytical data on known compounds and both liquid and solid detergent formulations.

Experimental

Bromocresol Green (BCG) Method for Anionic Actives

Reagents

Quaternary Hyamine 1622 solution (ca. 0.00450 N). About 2.1 g Hyamine 1622 (Rohm and Haas, mol and equivalent wt, 466.1) is dissolved in water, diluted to 1 liter, and standardized against dodecylbenzenesulfonic acid as described by House and Darragh (4).

Bromocresol Green indicator solution (buffered at pH 9.5). Prepared from 0.040 g bromocresol green (3′,3″,5′,5″-tetrabromo-m-cresolsulfonephthalein, Eastman 1782), 70 g sodium sulfate (CP), 3.09 g boric acid ("Baker Analyzed" Reagent), 34.4 meq of sodium hydroxide solution (0.5 N), sufficient Hyamine solution (ca. 13 ml 0.00450 N) to give zero titer for 10 ml distilled water, and water to make up to 1 liter.

Procedure

A weighed detergent sample (ca. 0.0025 equivalent of active) is dissolved in water and diluted to 250 ml. A 5-ml aliquot is placed in a 100-ml stoppered graduate cylinder with 5 ml water, 15 ml chloroform (CP), and 25 ml BCG solution and then titrated with Hyamine solution. The mixture is shaken vigorously after each increment of titrant. Initially the blue color of BCG concentrates in the aqueous (top) layer, and at the end point is equally distributed between the aqueous and chloroform layers. A correction curve for titers of less than 10 ml is given in Figure 1.

Calculation

$$\text{Milliequivalent anionic active/gram sample} = H \times F \times N_H \times 50/W$$

where H = ml Hyamine 1622 solution
F = correction factor from Figure 1
N_H = normality of Hyamine 1622 solution
W = sample wt in g

Amine Oxide Method

Reagents

Inorganic Salt solution (buffered). Same as BCG

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[1] Presented at the AOCS Meeting in Minneapolis, 1963.

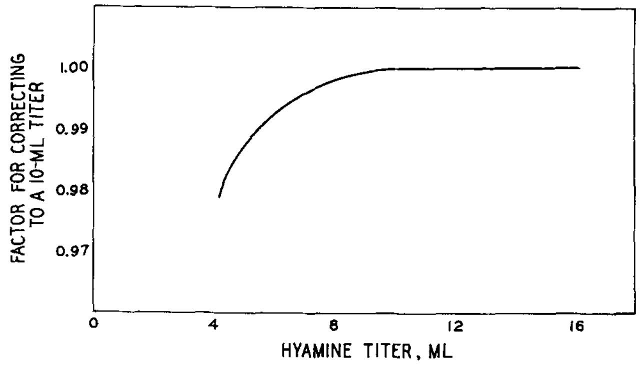

FIG. 1. Correction curve for quaternary titration of dodecylbenzenesulfonate with Hyamine 1622 solution and Bromocresol Green indicator.

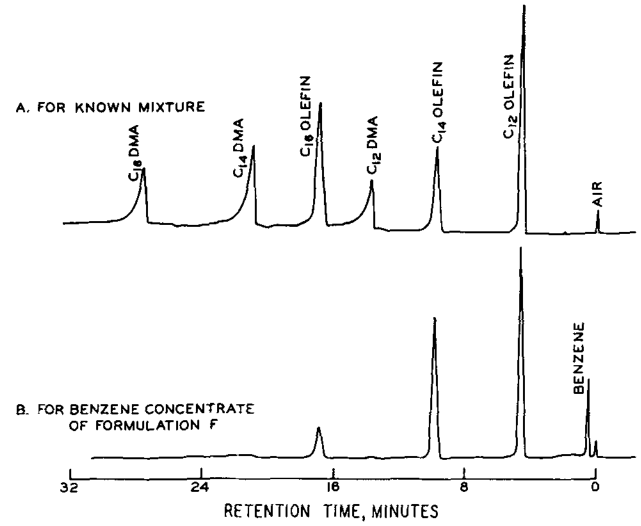

FIG. 2. Gas chromatograms of olefins and alkyldimethylamines.

Attenuation = 4X (except benzene = 64X).

solution, except BCG and Hyamine are omitted.

Methylene Blue (MB) indicator solution (pH 2). Prepare from 0.03 g methylene blue (Allied Chemical or equivalent), 12 g 96% sulfuric acid (CP), 50 g sodium sulfate (CP), and water to give 1 liter of solution.

Alkylbenzenesulfonate (ABS) solution. Dissolve 1.6 g commercial polypropylbenzenesulfonate (Oronite "Alkane 56" sulfonate or equivalent) in water, diluted to 1 liter, and standardize against Hyamine solution with MB or BCG indicator solution (ca. 0.00450 N).

Procedure

A 5-ml aliquot of solution (prepared for above BCG titration) is placed in a 125-ml separatory funnel (preferably with a Teflon stopcock). The stoichiometric amount of Hyamine solution (as determined by BCG titration) necessary to complex with anionic actives and 25 ml buffered inorganic salt solution is added. This mixture is extracted by vigorous shaking with a 10-ml, and then a 5-ml portion of chloroform.

Chloroform layers are separated and then combined in a 100-ml stoppered graduate cylinder. After the addition of 10 ml distilled water and 25 ml MB solution, the chloroform extract is titrated with ABS solution to an equal blue or equal intensity end point. The blue colors in the two layers do not always match perfectly, in which case the end point is taken at equal intensity.

Calculation (for 5-ml aliquot)

$$\text{Milliequivalent of amine oxide/g sample} = A \times N_A \times 50/W$$

where A = ml of ABS solution
N_A = normality of ABS solution
W = sample wt in g

Molecular Weight and Distribution of Amine Oxides by GLC Analysis

Conditions

Aerograph A-350-B chromatograph (Wilkens Instrument and Research, Inc.) with dual 10-ft x ¼-in. stainless steel columns packed with 20% "Apiezon" L on Chromosorb W (HMDS); helium rate, 50 ml/min; injector temp, 220C; column temp, programmed 180–280C at 4C/min.

Procedure

Two to five g detergent are extracted with 100 ml of 70% ethanol (basified to pH 9.5 with 6 N sodium hydroxide) and filtered; then 25 g anionic exchange resin (Dowex 1-X10 as hydroxide form from Dow Chemical Co.) are added to the filtrate and stirred for an hr. The mixture is slowly passed through a column (24-in. x ½-in. ID) packed with the same resin, and then the column is washed with 100 ml 70% ethanol (pH 9.5). The combined ethanol solution is concentrated carefully on a hot plate (ca. 150C surface temp) to 5 ml, diluted with 25 ml benzene, and finally concentrated to ca. 0.5 ml. Concn with benzene is to remove water, so the actual amount required depends on water content. If hazy, the concentrate is centrifuged to remove haze before a sample is injected into the gas chromatograph. In the chromatograph amine oxides are pyrolyzed to 1-olefins which are separated on the column. Olefin distribution is calculated from relative areas of olefin peaks on the chromatogram (Fig. 2-B) with corrections for differences in response factors (as determined on API or comparable olefin standards).

Amine oxide distribution and average molecular weight are then calculated from olefin distribution.

Results and Discussion

Bromocresol Green (BCG) Method for Anionic Actives

The BCG method for quaternary titration of anionic actives is a substantial improvement over the generally accepted methylene blue (MB) method (4) in the presence of amine oxides or appreciable amounts of low mol wt sulfonates. These materials interfere with the MB method but not the BCG method.

In the acidic MB indicator solution, amine oxides become cationic by proton addition and combine stoichiometrically with anionic actives present, so quaternary titration gives the differences between anionics and amine oxides instead of anionics alone. In the basic BCG indicator solution, amine oxides behave as nonionics and do not interfere with anionic determination.

Analysis of dodecylbenzenesulfonate in the presence of 50 wt % of low mol wt sulfonate by the BCG method results in an error of about 1% as compared to 27% (for p-xylenesulfonate) by the MB method (Table I). In several detergent formulations containing both low mol wt sulfonates and amine oxides BCG values for total anionic actives (Table

II) agree reasonably well with actual values (±4%).

Fatty acid soaps react partially with quaternary Hyamine, and affect the accuracy of the BCG method. Dodecylbenzenesulfonate in the presence of 50 wt % of sodium laurate gives a 13% higher active value. Normally, however, this is not a problem, since soap-amine oxide mixtures are uncommon.

In the absence of interfering substances, the MB and BCG methods give comparable values. Differences for dodecylbenzenesulfonate ("Alkane 56" sulfonate), nonylphenoxytriethoxyethanol sulfate ("Alipal CO-436"), and lauryl sulfate ("Sipex OP") are only 0.4%,0.8%, and 1.8% (based on MB values), respectively.

TABLE I

Bromocresol Green Versus Methylene Blue Method for Analysis of Dodecylbenzenesulfonate[a] in Presence of Low Molecular Weight Sulfonates

Low mol wt sulfonates (LMWS) (50 wt % based on dodecylbenzenesulfonate)	Bromocresol green method		Methylene blue method	
	Actual titer, ml	% Difference due to LMWS	Actual titer, ml	% Difference due to LMWS
None	13.50		13.55	......
Sodium benzenesulfonate	13.37	−1.0	....	......
Ammonium toluenesulfonate	13.53	−0.6	....	......
Sodium m-xylenesulfonate	13.52	+0.1	....	......
Sodium p-xylenesulfonate	13.56	+0.4	17.1–17.4[b]	+27
Sodium cumenesulfonate	13.65	+1.1	....	......

[a] "Oronite Alkane 56" sulfonate.

[b] End point is not sharp.

Amine Oxide Method

Determination of alkyldimethylamine oxides is based on separation (along with anionic actives as Hyamine complexes) from low mol wt sulfonates, followed by titration with standard ABS solution and acidic MB indicator. Under acidic conditions amine oxides are quantitatively titrated as quaternaries. Results for a series of experimental amine oxides with alkyl groups of 12–18 carbon atoms (Table III) agree quite well (±3.2%) with a recently published method based on potentiometric titration with alcoholic HCl (3). In detergent mixtures with experimental amine oxides or a commercial "cetyl" dimethylamine oxide, agreement between actual and found values is ±4.0% or better (Table II).

A sample size which gives a combined Hyamine (by BCG method for anionics) and ABS (by amine oxide method) titers of 10–20 ml is desired for accuracy and a sharp titration end point. In this range Hyamine titers of less than 10 ml require corrections (Fig. 1), but ABS titers do not.

Low mol wt sulfonates are extracted by a basic salt solution to avoid interference with MB titration. The basic solution keeps amine oxides in the nonionic form and thus increases their solubility in the chloroform layer. Before extraction, anionics are complexed with stoichiometric amounts of Hyamine to prevent them from solubilizing amine oxides into the aqueous phase. Titration of the aqueous phase after extraction shows only 2% unextracted amine oxide.

This method does not distinguish amine oxides from any alkyldimethylamines (Table III), their preparative precursors. However, the amines usually comprise less than 10% of the mixture, and are normally considered as part of the amine oxides added to detergents. As mentioned later, it might be possible to determine these amines separately by a GLC method.

Molecular Weight and Distribution of Amine Oxides

It was observed independently in our laboratory and by G. L. K. Hoh et al. (3) that amine oxides pyrolyze to olefins under certain gas chromatographic conditions. In our method, amine oxide mol wt and distribution are calculated from gas chromatograms of the derived olefins (Fig. 2-B). Analytical results for two experimental detergents agree reasonably

TABLE II

Analytical Results for Anionic Active and Amine Oxides in Detergent Formulations

Ingredients	meq/g[a]	Liquid formulation										Solid formulation	
		D		E		F		X		Y		Z	
		Wt %	meq/g	Wt %	meq/g	Wt %	meq/g	Wt %	meq/g	Wt %	meq/g	Wt %	meq/g
Alkylbenzenesulfonate[b]	2.69	15.36	0.413	14.64	0.394	16.10	0.433	15.42	0.415	15.90	0.428	15.36	0.413
Lauryl sulfate[c]	3.34	6.28	0.210	....		....		....	....	....		6.28	0.210
Lauryl sulfate[d]	2.39	....		....		....		6.82	0.163	....		....	
Nonylphenoxytriethoxyethanol sulfate[e]	1.16	....		16.22	0.188	17.00	0.197	....	....	16.82	0.195		
Xylenesulfonate		10.00		9.54		10.00		9.72		10.05		10.00	
"C_{12}" DMAO[f]	3.93	12.52	0.492	14.00	0.550	4.44	0.174	....				12.52	0.492
"C_{14}" DMAO[f]	3.63	....		9.22	0.335	3.37	0.122	....				....	
"C_{16}" DMAO[f]	3.24	....		....		1.10	0.036	....				....	
"Cetyl" DMAO solution[g]	0.773	....		....		....		48.50	0.375	40.15	0.310	....	
Nonionic[h]		....		4.87		....		....		5.00		....	
Ethanol		5.00		9.50		5.00		4.86		5.00			
Sodium tripolyphosphate		....		....		....		....		....		38.00	
"N" Silicate (solids basis)		....		....		....		....		....		4.50	
Sodium sulfate		....		....		....		....		....		8.30	
CMC		....		....		....		....		....		1.00	
"Additional" water		50.84		22.06		42.99		14.68		7.08		4.04	
Analysis													
Total anionic active (BCG Method), meq/g of formulation													
Actual		0.623		0.582		0.630		0.578		0.623		0.623	
Found		0.632,0.634		0.556,0.561		0.644,0.643		0.585		0.617		0.639	
% Average difference		+1.6		−4.0		+2.1		+1.2		−1.0		+2.6	
Total amine oxide (including amines), meq/g of formulation													
Actual		0.492		0.885		0.332		0.375		0.310		0.492	
Found		0.487,0.485		0.850		0.328.0.327		0.361		0.299		0.497	
% Average difference		−1.2		−4.0		−1.2		−3.7		−3.6		+1.0	

[a] Anionic active values are determined by BCG Method; DMAO values by ABS titration with MB indicator.

[b] "Oronite Alkane 56" sulfonate.

[c] "Sipon WD" (American Alcolac Corporation).

[d] "Sipex OP" (American Alcolac Corporation).

[e] "Alipal CO-436" (Antara Chemicals), 58% active solution.

[f] DMAO's are amine oxides prepared from redistilled commercial alkyldimethylamines (see Table III, footnote b for analyses).

[g] A commercial "cetyl" dimethylamine oxide solution (approximately 20%) from Onyx Chemical Corporation.

[h] "Igepal CO-630" (Antara Chemicals).

TABLE III

Anionic Titration Versus Acidimetric Method for Analysis of Amine Oxides (DMAO) and Amines (DMA)

	Acidimetric method			Anionic titration, meq (DMAO + DMA)/g	% Difference
	% DMAO	% DMA	meq (DMAO + DMA)/g		
Amine oxides[a]					
"C_{12}" DMAO	87.5	3.2	3.97	3.93	−1.0
"C_{14}" DMAO	83.0	7.1	3.53	3.63	+2.8
"C_{16}" DMAO	82.7	7.0	3.14	3.24	+3.2
"C_{18}" DMAO	82.9	7.4	2.90	2.99	+3.1
Amines[b]					
"C_{12}" DMA		100	4.67	4.41	−5.6
"C_{14}" DMA		100	4.15	4.06	−2.2
"C_{16}" DMA		100	3.73	3.59	−3.8
"C_{18}" DMA		100	3.37	3.30	−2.1

[a] Amine oxides prepared by H_2O_2 oxidation of the amines and analyzed by acidimetric method described in (3).

[b] Redistilled (under vacuum) commercial amines used in preparation of amine oxides. According to gas chromatographic analysis, average mol wt and per cent of principal dimethylamines (DMA) are as follows: for "C_{12}" DMA, 214, 1% C_{10}, 91% C_{12}, and 6% C_{14}; for "C_{14}" DMA, 241, 96% C_{14} and 2% C_{16}; for "C_{16}" DMA, 268, 2% C_{14} and 96% C_{18}; for "C_{18}" DMA, 296, 4% C_{16} and 96% C_{18}. Chromatographic conditions are: Aerograph gas chromatograph A-350-B; dual 10-ft x ¼-in. stainless steel columns, each packed with 20 g 20% "Apiezon" L on 60/80 Chromosorb W (HMDS); column temp 280C; injector temp, 240C; detector temp, 330C; and helium rate, 50 ml/min.

TABLE IV

Determination of Molecular Weight and Distribution of Alkyldimethylamine Oxides (DMAO) in Detergent Formulations by GLC

Amine oxide determination	Formulation E		Formulation F	
	Actual	Found	Actual	Found
Distribution				
C_{12} DMAO, wt %	62	64	51	49
C_{14} DMAO, wt %	38	36	37	40
C_{16} DMAO, wt %	....	....	12	11
Avg mol wt	239	238	245	245

well with actual values and are close to the generally expected accuracy of gas chromatographic methods (Table IV). These results indicate that pyrolysis is essentially complete or that the rate is fairly constant over the range of C_{12} to C_{16} alkyl chain.

Prior to analysis, samples are treated with anionic exchange resins to remove any alkyl sulfates which will partially decompose to olefins. Straight chain alcohols, on the other hand, do not decompose under these conditions. Treated samples are dried by refluxing with benzene before chromatographic analysis to minimize tailing. Prolonged heating with benzene should be avoided since amine oxides will decompose to olefins even under these mild conditions.

In chromatographic analysis of amine oxides, alkyldimethylamines do not decompose; and their peaks are well separated from olefin peaks as shown in Figure 2-A. Therefore, quantitative determination of the amines should be possible by the use of a suitable internal standard.

ACKNOWLEDGMENTS

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Dynamic Foam Test[1]

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Abstract

A test has been developed for measuring the amount of foam generated by a detergent composition under dynamic conditions and in the presence of sebaceous soil. Good correlation with actual practice results because the conditions of the test closely parallel practical laundry conditions.

Introduction

FOAM IS AN IMPORTANT criterion in the evaluation of detergent compositions. Since the design of a product is often centered upon foaming characteristics, it is important to be able to measure this interesting phenomenon under many conditions. Too much foam can be troublesome and not enough may also prove to be a disadvantage. The majority of housewives still relate cleaning ability to the presence of foam and this is not without some foundation. One cannot deny the aesthetic value of observing a washing machine smoothly cushioned under a "sea of foam" as compared to a sloshing interface that resembles a myriad of miniature tidal waves.

Many companies are now engaged in making detergents that are biodegradable. This whole problem has been highlighted because of the presence of foam in sewage. Part of the characterization of these new products must be a foam profile that relates them to existing products and to molecular configurations. Individual measurements such as film drainage, viscosity, density, spreading coefficients, etc., are helpful but somewhat meaningless in portraying the gross effects. The need arose, therefore, for a simple procedure for screening new alkylates and detergent compositions in general.

A review of the literature shows the Ross-Miles (10) test to be mentioned most frequently. This has been adopted by the ASTM. Another widely used procedure is the dishwashing test (12), used most frequently for screening light duty liquids. Weeks et al. (13) developed a test for hand-dishwashing compositions. Heinz and Machemer (5) used a mechanized disc and added emulsified fat together with street dust for correlating with the "washing tub." Barnett and Powers (1) mechanized a plunger and used sebum and sweat to test the performance of shampoos. Leenerts et al. (4) developed a technique utilizing a household washer for evaluation of foaming properties of hand-dishwashing detergents. More recently, Reich et al. (9) published a test designed for low foaming surfactants.

The writer wished to incorporate the following features into any screening procedure that might be workable:

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[1] Presented at the AOCS Meeting in Minneapolis, 1963.