Some New Developments in Surfactant Analysis

H.Y. LEW, Chevron Research Company, Richmond, California 94802

ABSTRACT

Three new analytical methods for surfactants have been developed and evaluated, and the stoichiometry in cationic titration of a dianionic surfactant has been determined. The three methods include: (a) a rapid method for pyrolytic cleavage of hydrophobic groups from surfactants to hydrocarbons, which can be used for quantitative identification of the hydrophobic groups; (b) a molecular weight method for alkylphenoxy and alkoxy polyethoxylates based on sulfation followed by cationic titration; and (c) a microcationic titration method designed for low levels (1-10 microequivalents) of anionic surfactants, which possesses certain advantages over conventional methods. Previously stoichiometry in cationic titration has been reported only for monoanionic surfactants. In a study of a dianionic surfactant, *n*-octadecylbutane 1,4-disulfate, each sulfate group was found to react in a 1:1 equivalent ratio with a cationic titrant.

INTRODUCTION

Surfactant analysis has grown to a very broad and intricate subject. Books, chapters and hundreds of articles have been written on the various aspects of surfactant analysis. Two of the most important aspects are the identification of a surfactant and the determination of the quantity of a surfactant. The four new developments discussed below deal with these two aspects.

A RAPID METHOD FOR CLEAVAGE OF HYDROPHOBIC GROUPS FROM SURFACTANTS FOR ANALYSIS

Application of tandem pyrolysis-gas chromatography (PGC) to surfactant analysis was first reported by Liddicoet and Smithson (1). They obtained "fingerprint" pyrograms at 650 C which served as qualitative identification of surfactants. This author (2) found that thermal and "acid" PGC at a lower temperature of 400-550 C essentially eliminated breaking of C-C bonds. Only C-S and C-O bonds were broken forming hydrocarbons representative of the hydrophobic portion of surfactant molecules. This method gave quantitatively the alkylbenzene carbon number and isomer distributions for linear alkylbenzene sulfonates and the olefin carbon numbers for alkyl sulfates, sulfonates and ethoxylates. However the tandem pyrolysis-chromatography combination had definite drawbacks. The narrow tubing connecting the pyrolyzer and chromatograph tended to plug; chromatographic peaks broadened when pyrolysis was not instantaneous; and the tandem arrangement only permitted GC analysis. By detaching the pyrolyzer from the chromatograph, it was possible to trap the liberated hydrocarbons for any analysis desired. Optimum conditions and applications found for this method are discussed in the following section.

Apparatus

The pyrolysis unit is shown in Figure 1. The pyrolyzer was the same as described previously (2). The stainless steel sample cup was 9/32 in. OD by 1/2 in. long with a well of 1/4 in. ID by 3/8 in. deep. Collector tubes were 3 mm OD by 7 in. glass tubings with a raised ridge around the tube 5-6 mm from the pyrolyzer end. "U"-shaped tubes immersed in a coolant bath were used for trapping light boiling pyrolyzates. The tube was attached to the pyrolyzer by a notched Swagelok nut with a Teflon back ferrule as a gasket (Fig. 1). Pyrolyzate solutions were evaporated in microtest tubes (8 mm OD by 1 3/4 in. and tapered at the bottom).

Procedure

For thermal pyrolysis a dry surfactant sample (1-50 mg) was weighed into a sample cup and pyrolyzed without additional chemicals. For "acid" pyrolysis about one to three times by weight of phosphorous pentoxide (P_2O_5) was added to the sample, mixed, and then 1-2 μl water

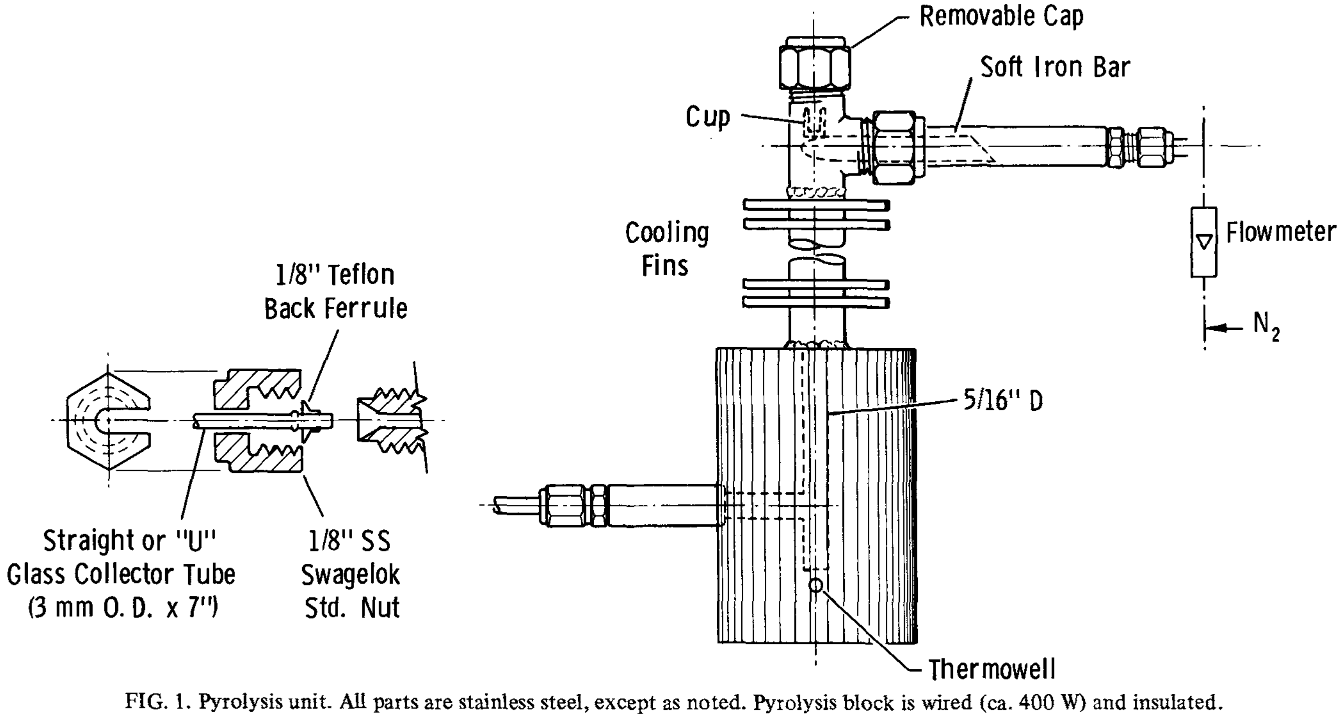

FIG. 1. Pyrolysis unit. All parts are stainless steel, except as noted. Pyrolysis block is wired (ca. 400 W) and insulated.

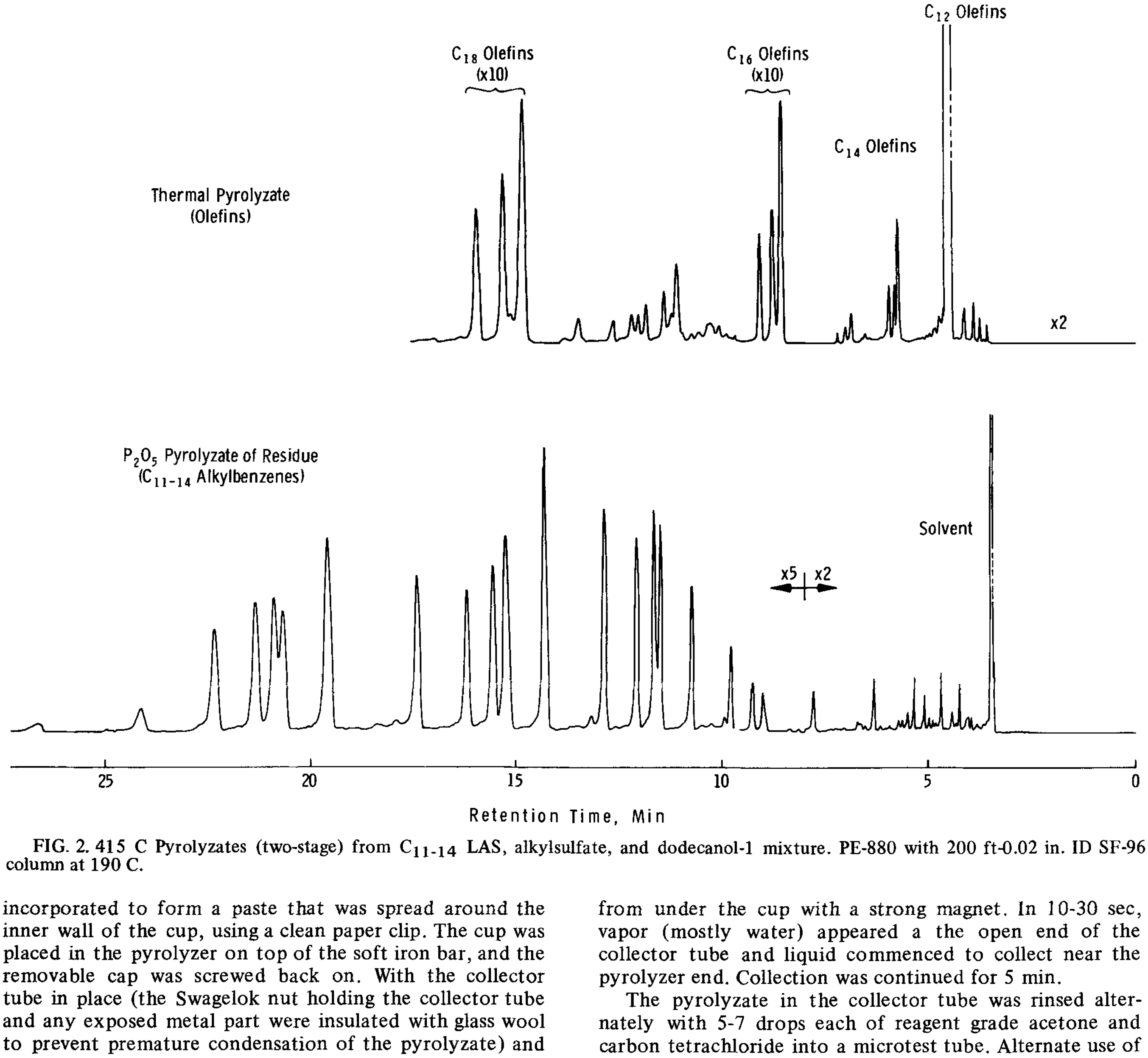

FIG. 2. 415 C Pyrolyzates (two-stage) from C_{11-14} LAS, alkylsulfate, and dodecanol-1 mixture. PE-880 with 200 ft-0.02 in. ID SF-96 column at 190 C.

incorporated to form a paste that was spread around the inner wall of the cup, using a clean paper clip. The cup was placed in the pyrolyzer on top of the soft iron bar, and the removable cap was screwed back on. With the collector tube in place (the Swagelok nut holding the collector tube and any exposed metal part were insulated with glass wool to prevent premature condensation of the pyrolyzate) and nitrogen flowing at 5 ml/min, the cup was dropped into the pyrolyzing chamber (usually 400-415 C) by moving the bar from under the cup with a strong magnet. In 10-30 sec, vapor (mostly water) appeared a the open end of the collector tube and liquid commenced to collect near the pyrolyzer end. Collection was continued for 5 min.

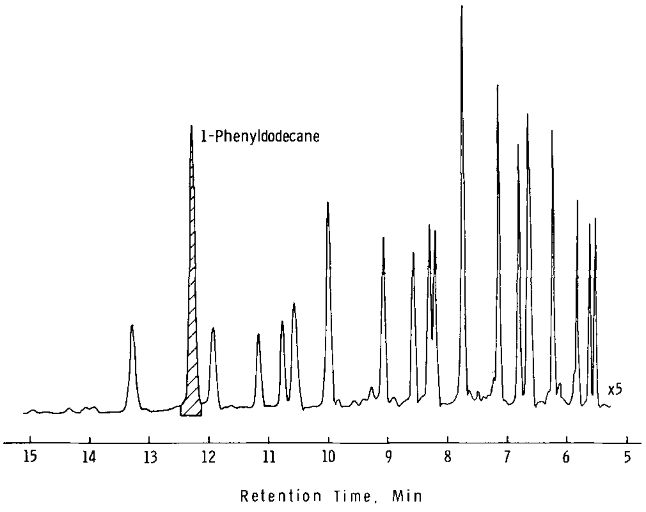

FIG. 3. 400 C P_2O_5-Pyrolyzate of 1-phenyldodecane sulfonate and C_{10-13} LAS after thermal pyrolysis of C_{15-18} AOS. PE-880 with 200 ft-0.02 in. ID SF-96 column, temperature-programed 100-200 C at 10 C/min.

The pyrolyzate in the collector tube was rinsed alternately with 5-7 drops each of reagent grade acetone and carbon tetrachloride into a microtest tube. Alternate use of the two solvents removed both water and hydrocarbon drops from the collector tube. The solvent was carefully evaporated by placing the microtest tube in a 25 ml beaker of hot water. Then the sides of the test tube were rinsed down with a few drops of carbon tetrachloride and the carbon tetrachloride evaporated to leave the hydrocarbon pyrolyzate. The last addition and evaporation of carbon

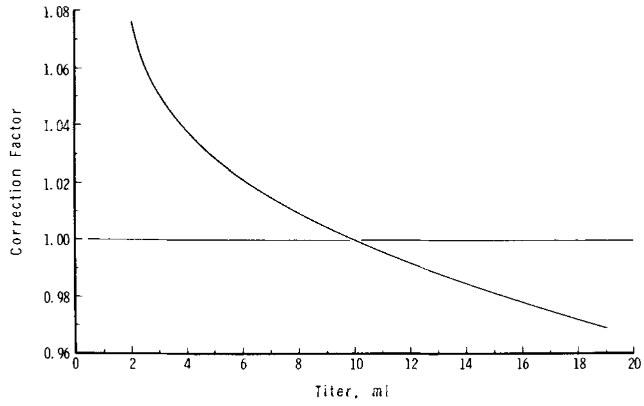

FIG. 4. Correction curve for titration of sulfated ethoxylates (with 0.00467 N Hyamine).

TABLE I

Mass Spectral Analyses of P_2O_5-Pyrolyzate from a Branched Alkylbenzene Sulfonate and of the Branched Alkylbenzene Precursor

Analysis	Branched alkylbenzene precursor	415 C P_2O_5-Pyrolyzate[a]	415 C P_2O_5-Pyrolyzate[b]
Alkylbenzene distribution, mol %, number of C in side chain			
9	3.1	2.0	2.3
10	2.8	2.3	2.4
11	6.4	5.9	6.0
12	30.6	30.6	30.5
13	14.3	14.8	14.5
14	13.1	13.6	13.6
15	23.5	24.8	24.7
16	4.3	4.4	4.5
17	1.3	1.2	1.2
18	0.4	0.4	0.3
19	0.2	—	—
Average mol wt	262.4	263.6	263.3

[a] From corresponding sulfonate (5-10 min concentration).

[b] From corresponding sulfonate after 2 hr concentration.

tetrachloride azeotropically removed any trace of moisture. With a gentle stream of nitrogen or air, the solvent is removed completely in 5-10 min.

The pyrolyzate can now be analyzed by IR, GC, mass spectrometry (MS), or any other techniques desired. Examples will be given for GC and MS to show the accuracy of the method.

Results and Discussion

The pyrolyzate produced by this method can be used for obtaining quantitative data on the hydrophobic portion of a surfactant. Alkyl sulfates and sulfonates and alkoxy- and alkylphenoxy ethoxylates were pyrolyzed either thermally or with P_2O_5, as the acid, to give olefins; whereas alkylbenzene sulfonates (ABS) pyrolyzed significantly at 400-550 C only with P_2O_5 and gave alkylbenzenes. The mass spectral analysis in Table I illustrates how well the pyrolyzate from a branched alkylbenzene sulfonate agrees with the alkylbenzene precursor in carbon number distribution and average molecular weight. The data in the last column show that the alkylbenzene distribution of the pyrolyzate was not affected significantly by increasing the time for concentration from the normal 5-10 min to 2 hr. However low boiling hydrocarbons will undoubtedly be affected.

Application of this method to linear alkylbenzene sulfonate (LAS) shows good agreement between the pyrolyzate and alkylbenzene precursor (Table II) in carbon number, average molecular weight and isomer distribution.

In a typical detergent mixture containing alkyl sulfate (AS), LAS and dodecanol-1 (as foam additive), the alkyl sulfate (also dodecanol-1) could be pyrolyzed thermally to produce olefins (Fig. 2), and then the residual LAS could be pyrolyzed with P_2O_5 to produce alkylbenzenes. From the chromatograms of the pyrolyzates from this two-stage pyrolysis, there did not appear to be any problem with interfering peaks (Fig. 2). Also, olefin (Table III) and alkylbenzene (Table IV) analyses agreed quite well with expected values.

The LAS content in a LAS/alpha olefin sulfonate (AOS) detergent formulation could be estimated by adding a known amount of 1-phenyldodecane sulfonate, equal to ca. 10% of the LAS, as an internal standard. To assure maximum accuracy, a minimum of ca. 0.020 g internal standard was used. The sample of the formulation and standard were dissolved in water and dried to assure a uniform mixture. A sample of this mixture was first thermally pyrolyzed to eliminate the AOS and minimize interference, and the residue was then pyrolyzed with P_2O_5. In the chromatogram of the P_2O_5-pyrolyzate (Fig. 3), only alkylbenzene peaks appeared; none of the olefin peaks from AOS were present. The amount of LAS was calculated from the relative areas of LAS alkylbenzenes and 1-phenyldodecane.

Values of 19.4-20.4% LAS were obtained in four separate pyrolyses as compared to 21.0% for the make-up LAS/AOS blend. In this two-stage pyrolysis, it was necessary to vent the pyrolyzer between the thermal and P_2O_5 pyrolysis to remove traces of olefins from AOS; also, for best GC results, the 1-phenyl-dodecane peak should be 30-70% of full scale.

Thus this method provides a rapid mean of obtaining a hydrocarbon that could be used for quantitative determination of the hydrophobic group. With a dry surfactant sample, it requires only 20-30 min.

A MOLECULAR WEIGHT METHOD FOR ALKYLPHENOXY- AND ALKOXYPOLYETHOXYLATES

Average molecular weights can be quite valuable in the identification of an alkylphenoxy- or alkoxypolyethoxylate surfactant. Among chemical methods available for their determinations are hydroxyl number by acetylations (3) and active hydrogen by the Zerewitinoff method (4,5). However, with these methods, a few per cent of low molecular weight alcohol, glycol or polyglycol, which are often present in mixtures with ethoxylate surfactants, can produce a considerable error in molecular weight. The

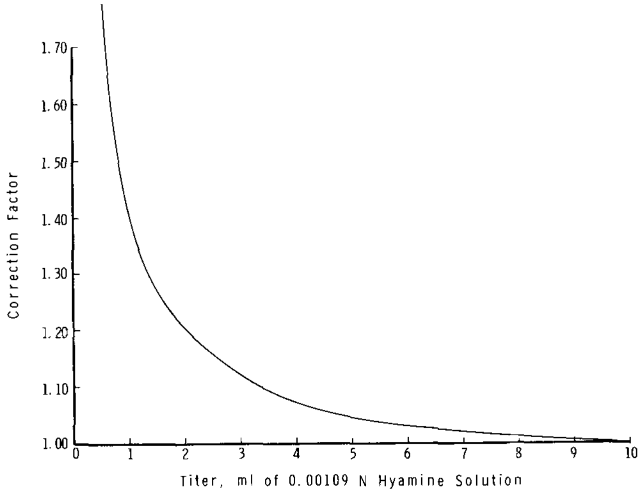

FIG. 5. Correction curve for titration of branched ABS using 0.00109 N Hyamine.

TABLE II

Gas Chromatographic Analyses[a] of P_2O_5-Pyrolyzate from a Linear Alkylbenzene Sulfonate and of the Linear Alkylbenzene Precursor

Linear alkylbenzene (LA) side chain and isomer distribution, wt %	C_{11}-C_{14} Linear alkylbenzene precursor	415 C P_2O_5-Pyrolyzate from corresponding sulfonate
C_{10}		
2φ	---	---
3φ	—	—
4φ	—	---
5φ	0.1	0.1
C_{11}		
2φ	3.7	3.6
3φ	1.7	1.8
4φ	1.1	1.1
5φ and 6φ	1.0	1.0
C_{12}		
2φ	9.7	9.5
3φ	5.8	6.0
4φ	5.2	5.3
5φ and 6φ	10.8	10.9
C_{13}		
2φ	9.7	9.4
3φ	5.9	5.9
4φ	5.2	5.2
5φ, 6φ and 7φ	14.3	14.4
C_{14}		
2φ	—	0.2
3φ	1.0	1.0
4φ	5.7	5.7
5φ, 6φ and 7φ	19.1	18.9
Average mol wt	257.1	257.0
LA Isomers, wt % of LA		
2φ	23.1	22.7
3φ	14.4	14.7
4φ	17.2	17.3
5φ, 6φ and 7φ	45.3	45.3

[a] PE-880 with 200 ft, 0.02 in ID SF-96 column at 190 C.

method that will be described in the second section of this paper is only slightly affected by these compounds. It is based on quantitative sulfation of the ethoxylate with chlorosulfonic acid according to the following equation: $R\text{-}O(CH_2CH_2O)_xH + ClSO_3H \rightarrow RO(CH_2CH_2O)_x\ SO_3H + HCl$ followed by cationic titration of the anionic formed.

Solutions

A 0.004 N Hyamine 1622 solution was used and also a methylene blue indicator solution of 0.03 g methylene blue hydrochloride, 12 g sulfuric acid (98%) and 50 g sodium sulfate (anhydrous) diluted to 1 liter with distilled water.

Procedure

In a dry 125 ml Erlenmeyer flask was weighed accurately 0.2000-0.5000 g (ca. 400 microequivalent) of ethoxylate. Then 40 ml anhydrous ethyl ether (reagent grade) was added to dissolve the sample, with warming if necessary. The ether solution was cooled in an ice bath, and 0.5 ml of fresh chlorosulfonic acid added slowly from a 6-8 in. glass disposable pipette (fitted with a rubber bulb and marked to deliver 0.5 ml) with the tip immersed in the ether solution. The tip was kept moving around during the addition to prevent local heating and excessive sputtering. With the bulb removed, the pipette was rinsed with a few milliliters of dry ether which was allowed to drain into the ether solution. The flask was then removed from the ice bath and carefully swirled, and its walls were rinsed down with 5-10 ml ether. After standing 5 min at room temperature for sulfation to be completed, the solution was cooled in an ice bath and neutralized with 4N NaOH to a definite pink color with phenolphthalein indicator. The neutralized solution was evaporated in a hot water bath (50-60 C) to remove ether (solution should still be pink), diluted to 100 ml in a volumetric flask, and a 10 ml aliquot was titrated with a standardized cationic (ca. 0.004 N Hyamine 1622) solution using a methylene blue indicator (6). The titer was corrected using the curve in Figure 4.

TABLE III

Gas Chromatographic Analysis[a] of Thermal Pyrolyzate from LAS/AS/C_{12}-OH[b]

	Olefin distribution, %	
Olefin chain length	GC[c] Analysis of alcohol from AS	415 C Thermal pyrolyzate from LAS/AS/C_{12}-OH
C_{14}	1.5	1.8
C_{15}	0.8	0.4
C_{16}	31.1	29.6
C_{17}	3.4	3.0
C_{18}	63.2	65.2
Average mol wt	241.6	242.0

[a] PE-880 with 200 ft, 0.01 in. ID SF-96 at 190 C.

[b] LAS/AS/C_{12}-OH = Blend of linear alkylbenzene sulfonate alkyl sulfate/dodecanol-1.

[c] GC = Gas chromatographic.

Results and Discussion

For accurate determinations, apparatus and ether must be dry, and chlorosulfonic acid must be fresh and preferably distilled. Sputtering on contact with the ethoxylate solution and absence of a small lower sulfuric acid layer after sulfation are evidences of a fresh acid.

Average molecular weights determined for a number of alkylphenol and alkoxyethoxylates are tabulated in Table V. For most ethoxylates the average deviation is less than 4% of the calculated value. Larger deviations of up to 11.5% were obtained for those with longer ethoxylate chains, e.g., Igepal CO-710 and Tergitol 12-P-12.

Once the molecular weight is determined, only the size of the alkyl chain on the alkylphenoxy or alkoxy group is needed for calculating the polyethoxy chain. The "acid" pyrolysis method described in the first section of this

TABLE IV

Gas Chromatographic Analysis[a] of P_2O_5-Pyrolyzate of Residue Following Thermal Pyrolysis of LAS/AS/C_{12}-OH[b]

Linear alkylbenzene (LA) side chain and isomer distribution, wt %	Alkylbenzene precursor of LAS	415 C P_2O_5-Pyrolyzate of residue after thermal pyrolysis of LAS/AS/C_{12}-OH mixture
C_{10}	0.1	0.1
C_{11}		
2φ	3.7	3.6
3φ	1.7	1.8
4φ	1.1	1.1
5φ and 6φ	1.0	1.1
C_{12}		
2φ	9.7	9.2
3φ	5.8	6.3
4φ	5.2	5.3
5φ and 6φ	10.8	10.9
C_{13}		
2φ	9.7	8.9
3φ	5.9	6.4
4φ	5.2	5.4
5φ, 6φ and 7φ	14.3	14.1
C_{14}		
2φ	—	0.6
3φ	1.0	1.4
4φ	5.7	5.5
5φ, 6φ and 7φ	19.1	18.3
Average mol wt	257.1	257.0
LA Isomers, weight % of LA		
2φ	23.2	22.4
3φ	14.4	15.9
4φ	17.2	17.3
5φ, 6φ and 7φ	45.2	44.4

[a] PE-800 with 200 ft, 0.02 in. ID SF-96 column at 190 C.

[b] See footnote b, Table III.

paper, followed by GC or mass spectral analysis, will provide this information. The size of the alkoxy group can also be determined by Lee and Puttnam's method based on GC analysis of iodo derivatives of the alkyl group in alcohol ethoxylates (7).

This procedure can also be used for product control to check the amount of ethylene oxide added during ethoxylation. However, because of its sensitivity to moisture, extreme care is required.

MICROCATIONIC TITRATION METHOD

A cationic, or two-phase titration (6), is normally carried out on ca. 50 microequivalent (μeq) of anionic surfactants with a standard cationic solution, such as Hyamine 1622, of ca. 0.004 N. Edwards and Ginn (8) developed a two-phase titration method employing azophloxine indicator for determination of 1-50 ppm (ca. 0.003-0.15 μeq) Nacconol detergent for sewage analysis; and Reid et al. (9) reported satistactory use of "mixed indicator" for 2-20 ppm (ca. 0.01-0.1 μeq) of lauryl sulfate. The method that will be described in the third section of this paper was originally developed for an intermediate range of 1-10 μeq anionic surfactant to study detergent concentrations in wash solutions or adsorption on washed fabrics, or both, as related to detergency. However it was found to offer advantages over the normal method (6) for certain detergent blends as mentioned under Results and Discussion.

Solutions and Equipment

A 0.00100 N standard Hyamine 1622 solution containing 0.006% Igepal CO-630 as a wetting agent was used. A 0.00100 N standard anionic active solution, was also used, and a methylene blue indicator solution of 0.03 g methylene blue hydrochloride, 12 g sulfuric acid (98%) and 50 g sodium sulfate (anhydrous) diluted to 1 liter with distilled water.

Procedure

A 10 ml aliquot of a sample solution containing 1-10 μeq anionic active, 15 ml chloroform and 25 ml methylene blue indicator solution was titrated with the 0.00100 N standard Hyamine 1622 solution from a 5 or 10 ml buret by the usual shaking technique (6). The end point was taken as the point at which the color intensities in the aqueous and chloroform layers were equal when viewed by the transmitted light from a fluorescent titration lamp.

For titers of more than 2 ml, correction factors such as shown for branched alkylbenzene sulfonate (ABS) in Figure 5 may be used. For titers of less than 2 ml, a fixed volume correction or blank, determined by titrating 10 ml water with 0.00100 N standard anionic-active solution, is preferred. This volume corresponds to the amount of anionic required for the formation of sufficient chloroform-soluble methylene blue-anionic surfactant complex to produce equal color intensities in the two layers.

Calculations

Using correction factors:

$$\%\ \text{Anionics} = \frac{\text{ml}_{\text{Hyamine}} \times \text{N} \times \text{Eq Wt} \times \text{Correction Factor}}{100}.$$

Using fixed volume correction ([a]Titer for water blank.):

$$\%\ \text{Anionics} = \frac{(\text{ml}_{\text{Hyamine}} + \text{ml}^{a}{}_{\text{Anionic}}) \times \text{N} \times \text{Eq Wt}}{100}.$$

Results and Discussion

The correction curve shown in Figure 5 for branched alkylbenzene sulfonate (ABS) can also be used for linear alkylbenzene sulfonate. The "fixed" volume correction, which was usually ca. 0.50 ml of 0.001 N anionic solution, corrects titers accurately up to at least 10 ml (larger titers were not checked). The latter is preferable for 2 ml and lower titers, since the correction curve is very steep below 2 ml.

TABLE V

Average Molecular Weight of Alkylphenoxy and Alkoxy Ethoxylates by the Sulfation Method

Ethoxylate	Mol wt		Average deviation from calculated value, %
	Calculated[a]	Found	
Igepal CO-430	386	385, 386	0.0
Igepal CO-610	560	552, 546	2.0
Igepal CO-630	595	590, 589	0.1
Igepal CO-710	759	667, 667	11.5
Experimental P-9-7.3	541	535, 546, 540	0.6
Experimental P-9-9.6	642	648, 652	1.3
Experimental P-9-12.9	788	758, 759, 754	3.9
Tergitol 12-P-6	526	530, 539	2.0
Tergitol 12-P-9	658	631, 629	4.2
Tergitol 12-P-12	790	737, 730	7.0
Igepal CA-630	557	569, 572	2.3
Neodol 25-3	339	350, 352	3.5
Neodol 25-7	510	526, 530	3.5

[a] Values for Igepal, Tergito and Neodol ethoxylates were calculated from data in manufacturer's brochure, and those for experimental ethoxylates from weight of ethylene oxide added. In code for experimental ethoxylates, "P-9" designates a C_9 polypropylene side chain and last number, the number of ethylene oxide units.

Values obtained by this method agreed quite well with the normal method (6) using 0.004 N Hyamine solution and samples containing ca. 50 μeq of anionics.

One advantage for the microcationic method is its relative insensitivity to high concentrations of toluene sulfonate. For mixtures of equal weights of toluene sulfonate and ABS, the correction factor for a 5 ml titer by the microcationic method was only 0.99 as compared to 0.77 for the normal method. Also, for certain anionic-nonionic detergent formulations containing a high proportion of nonionics, titration was almost impossible by the normal method because of a very stable emulsion but was carried out with ease by the micromethod.

STOICHIOMETRY IN CATIONIC TITRATION OF A DIANIONIC SURFACTANT

The stoichiometry in cationic titration of a surfactant with more than one anionic group has not been reported in the literature. Possible variables that might affect the stoichiometry for polyanionic surfactants are the proximity of the anionic groups or the length of the hydrophobic group, or both. The final section of this paper covers the synthesis and the stoichiometry of 2-octadecylbutane 1,4-disulfate, a dianionic surfactant. Hopefully these results will stimulate other investigations on cationic titration of polyanionic surfactants.

Synthesis

Disodium and calcium 2-octadecylbutane 1,4-disulfates were synthesized starting with *n*-octadecyl succinic anhydride (from Humphrey Chemical Co.). The anhydride was reduced with lithium aluminum hydride in tetrahydrofuran at 65 C to the butane 1,4-diol. After recrystallization from methanol, the diol was sulfated with chlorosulfonic acid in methylene chloride at 10-15 C. The disodium and calcium salts were obtained by neutralizing the sulfated diol with sodium hydroxide and calcium hydroxide, respectively, and recrystallizing from 80% aqueous ethanol.

Analysis

Karl Fischer water analysis, Leco sulfur analysis and an equivalent weight determination indicated the disodium salt to be a disulfate-dihydrate (calculated for $C_{22}H_{44}S_2O_8Na_2 \cdot 2H_2O$: H_2O, 6.2; S, 11.0; equivalent weight, 291. Found: H_2O, 6.4; S, 11.2; equivalent weight, 289).

The equivalent weight was determined by an acid hydrolysis method in which each equivalent of alkyl sulfate was hydrolyzed to an alcohol and one equivalent of sodium bisulfate; base titration of the sodium bisulfate formed gave the number of sulfate groups in the molecule. In the actual method, a 0.5 g sample was hydrolyzed with 0.05 N H_2SO_4 for 22 hr. Absence of anionic active (by cationic titration) in an aliquot of the sample indicated the hydrolysis was complete. Bisulfate was determined by potentiometric titration. Similar methods are discussed by Rosen and Goldsmith (10).

Results and Discussion

Normal cationic titration of the disodium salt with 0.004 N Hyamine 1622 and methylene blue indicator indicated that each of the sulfate groups reacts stoichiometrically with one equivalent of cationic surfactant such as Hyamine 1622. Equivalent weight, as determined by cationic titration, was 293, as compared to the theoretical value of 291 for the disulfate-dihydrate. The calcium salt equivalent weight by cationic titration also supported the one to one relationship (288 vs. a theoretical of 288 for the dihydrate).

These results show that a C_{22} surfactant with two anionic sulfate groups separated by four carbon atoms titrates with one equivalent of cationic surfactant for each of its sulfate groups. Further investigation is needed to determine the effect of distance, if any, between anionic groups, total carbon atoms and more than two anionic groups.

ACKNOWLEDGMENTS

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