Analytical Methods for Alpha Sulfo Methyl Tallowate

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Recent economic trends have made sulfo methyl tallowates viable alternatives to oil-based synthetic detergents in certain applications. Currently available analytical methods to monitor and control product quality are rather limited and sketchy, however, meaning that a substantial amount of methods development has been required. This includes methodology for resolving the three types of sulfonates present, and for the determination of sodium methyl sulfate.

This paper describes new methods developed for making these determinations. They include a new two-phase dye transfer titration and a potentiometric ion-selective electrode titration for the resolution of sodium alpha sulfo tallowate and sodium alpha sulfo tallow acid. In addition, a new method involving saponification and two-phase dye transfer or potentiometric ion-selective electrode titrations for the determination of sodium methyl sulfate is described.

Alpha sulfo methyl tallowates have a unique combination of desirable properties, including biodegradability, hydrolytic stability and biological compatibility. Also, since their feedstock costs and availability seem to be more stable than those of petroleum-based feeds, their potential use in detergent powders (particularly non phosphate heavy duty laundry), liquid formulations and detergent bars is considerable.

Analytical methods reported in the literature (1-5) to monitor and control product quality are rather limited and sketchy, however, and a substantial amount of methods development has been required. This included methodology for resolving the three types of sulfonates present (a, b, c) and for the determination of sodium methyl sulfate (d) (Fig. 1).

This paper describes new methods developed in the analytical laboratories of the Stepan Co. for making these determinations, and also for doing a compositional analysis of the finished product. It is intended that these determinations be done rapidly, using ordinary, inexpensive laboratory equipment in a quality control/quality assurance environment.

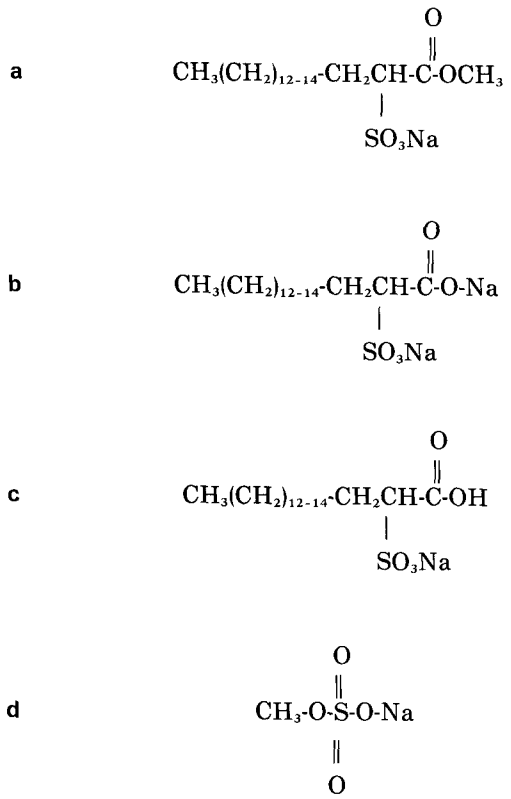


FIG. 1. Structures for the three sulfonates present in alpha sulfo methyl tallowate, and for sodium methyl sulfate. a, Monosodium alpha sulfomethyl tallowate; b, disodium alpha sulfo tallowate; c, monosodium alpha sulfo tallow acid, and d, sodium methyl sulfate.

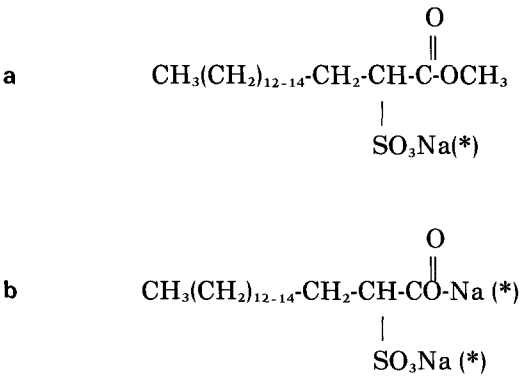
ANIONIC ACTIVES CONTENT

A new method for the determination of the three types of sulfonate actives was developed by performing four tests. These were:

- Two-phase cationic titration using phenol red indicator.
- Two-phase cationic titration using methylene blue indicator.
- Acid value.
- Free fatty matter.

The two-phase titration using phenol red is adapted from a method by Han (6), while that using methylene blue is based on a procedure originally developed by Epton (7). In both titrations, 0.004 N Hyamine 1622 (a quaternary ammonium surfactant available from Lonza, Inc., Fair Lawn, New Jersey) solution was used as the titrant.

The Hyamine-phenol red (HPR) titration, because it is carried out using a phosphate solution at a pH of about 9.0, determines both sulfonates and carboxylate functionalities, as depicted by the following, in which (*) indicates the functional group titrated:



c $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (*))\text{-}C(=O)\text{-}OH(*)$

d $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (*))\text{-}C(=O)\text{-}OH(*)$

e $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (*))\text{-}C(=O)\text{-}O\text{-}Na(*)$

This titration has two advantages over the two-phase bromcresol green method of Lew (8) in this application. Because phenol red is a low molecular weight anionic dye, it permits the titration to be more responsive to lower molecular weight surfactants (6). Also, because the end point taken is that where the first pink color appears in the bottom (chloroform) layer, the problem of trying to match colors in two layers does not exist, as it does in the bromcresol green procedure. However, because the small amount of unsulfonated fatty acids and sodium soaps present are also titrated, corrections should be made for these. This can be accomplished by doing petroleum ether extractions and acid value, as will be shown later.

The Hyamine-methylene blue (H-MB) titration is performed in acid medium; therefore, the RCOOH group is protonated and no longer available for titration as an anionic. This means that only the sulfonate group is titratable in this method:

a $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (**))\text{-}C(=O)\text{-}O\text{-}CH_3$

b $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (**))\text{-}C(=O)\text{-}O\text{-}Na$

c $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na\ (**))\text{-}C(=O)\text{-}O\text{-}H$

where (**) designates the functional group titrated.

It should be mentioned that slight water insolubility problems observed were cleared up by the addition, drop by drop, of a small amount of Makon 10 [Stepan's ethoxylated (10 mole) nonylphenol] without affecting the two-phase titration values.

TABLE 1

Determination of Sulfonated and Unsulfonated Tallow Acid

A. *Acid value determines (in me/g)*

1. $CH_3\text{-}(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na)\text{-}COOH$ plus

2. $CH_3\text{-}(CH_2)_{12-14}\text{-}CH_2\text{-}CH_2\text{-}COOH$

B. *Pet ether extraction (PEX) determines*

1. $CH_3(CH_2)_{12-14}\text{-}CH_2CH_2\text{-}COOH$ plus

2. $CH_3(CH_2)_{12-14}\text{-}CH_2CH_2\text{-}COOCH_3$

C. *Titration of PEX determines*

$CH_3(CH_2)_{12-14}\text{-}CH_2CH_2\text{-}COOH$ (in me/g)

D. *Acid value (me/g) minus c (me/g)* =

$CH_3(CH_2)_{12-14}\text{-}CH_2CH(SO_3Na)COOH$

E. *PEX at pH3 determines*

$CH_3(CH_2)_{12-14}\text{-}CH_2CH_2\text{-}COONa$ as its fatty acid

Table 1 illustrates how alpha sulfo tallow acid (and free tallow acid) are determined. The acid value is determined on a 10-g sample dissolved in 50-100 ml of neutral 3A alcohol. This is titrated with standard NaOH to the phenolphthalein end point, and the result calculated in me/g. This determines both acids. Petroleum ether extraction (PEX) from alcohol water solution extracts free tallow fatty acid plus free methyl tallowate. Titration of the extract with standard NaOH affords me/g free tallow acids (AVPEX), and subtraction of this titration from the acid value (AV) yields the monosodium alpha sulfo tallow acid.

Dropping the pH of the alcohol water solution and further extracting with petroleum ether yields sodium soaps as their fatty acids. To summarize how the percentage of the three sulfonated entities are calculated:

a $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na)\text{-}COO\text{-}CH_3$,

$$\% = (2HMB - HPR)\ (\text{meq wt})\ (100)$$

b $CH_3(CH_2)_{12-14}\text{-}CH_2\text{-}CH(SO_3Na)\text{-}COO\text{-}Na$,

$$\% = (HPR - HMB - AV)\ (\text{meq wt})\ (100)$$

c $CH_3(CH_2)_{12-14}$-CH_2-CH-COOH,
|
SO_3Na

$$\% = (AV - AVPEX)\ (meq\ wt)\ (100)$$

Since Hyamine methylene blue titrates only sulfonates and Hyamine phenol red determines both sulfonates and carboxylates, subtraction of the HPR me/g from double the HMB me/g yields only monosodium alpha sulfo methyl tallowate, because this is the only species with only the sulfonate function. Disodium alpha sulfo tallowate is equal to the HPR (carboxylates + sulfonates) minus HMB (sulfonates) minus acid value (sulfonated plus unsulfonated carboxylates). Finally, the monosodium alpha sulfo tallow acid content is equal to the acid value (sulfonated plus unsulfonated carboxylates) minus the acid value of the petroleum ether extract (unsulfonated carboxylates).

The theory that Hyamine phenol red is effective for carboxylate determination was tested by titrating a sample of tallow fatty acid with standard NaOH to phenolphthalein, then comparing this result with that obtained by the HPR method on the same sample. This comparison is given in Table 2.

The close agreement shown in Table 2 indicates that the HPR method is quite effective for soap determination, and therefore should be an effective tool for determining carboxylate content in alpha sulfo methyl tallowates and their saponification products.

SODIUM METHYL SULFATE

A new method for the determination of sodium methyl sulfate by saponifying the sample and correcting for the increase in soap content has been developed. The determination may be performed according to this general outline:

- Perform Hyamine phenol red on a sample; record me/g as HPR.
- Reflux a separate sample (ca. 3 g sulfonate active) with 50 ml 0.5N KOH in ethylene glycol for 30 min along with a blank.
- Titrate sample + blank to phenolphthalein end point with 0.5 N H_2SO_4. Calculate saponification value in me/g as S.V.
- Perform Hyamine phenol red on saponified sample. Record me/g as HPRSAP.
- Calculate sodium methyl sulfate content % CH_3SO_4Na = (S.V. + HPR − HPRSAP − FME) (me/g) (13.4) where FME = free methyl esters = PEX − AVPEX (usually small, usually can be ignored).

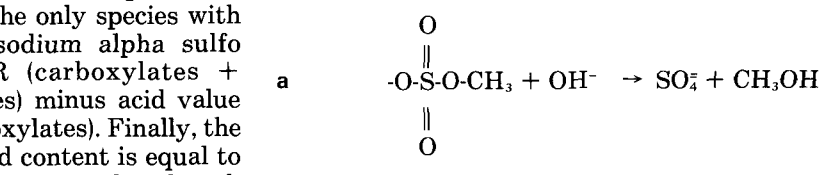
The new method for the determination of sodium methyl sulfate is based on the finding that this substance is completely converted to inorganic sulfate by refluxing with 0.5N KOH in ethylene glycol for 30 min. The reaction is given in Figure 2. It was verified by refluxing Kodak potassium methyl sulfate (EK#853, 97% minimum purity by sulfated potassium ash) along with a blank, for varying lengths of time, with 50 ml of 0.5N KOH in ethylene glycol. The percent CH_3OSO_3K determined was measured as a function of time and compared to theory.

Table 3 shows the results of this study. While the

TABLE 2

Soap Determination by HPR Method Compared to Acid Value

Trial	A.V., me/g	HPR me/g
1	3.484	3.303
2	3.484	3.344
3	3.478	3.333

a


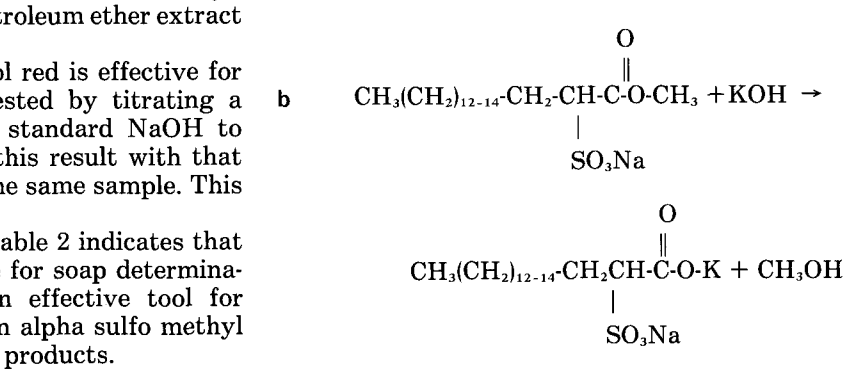
b


FIG. 2. Equations for the saponification of sodium methyl sulfate and sodium alpha sulfo methyl tallowate.

TABLE 3

Saponification of 97% Minimum Pure Potassium Methyl Sulfate as a Function of Time

Reflux Time (min)	% CH_3SO_4K
30	98.56
60	98.89
120	99.32
240	99.92

hydrolytic stability of alpha sulfo methyl tallowate is well established, the stability of this product under the conditions (high pH, high temperature) of this test was unknown.

It is probable that the reaction given in Figure 2b takes place at least in part. To monitor and correct for the saponification of the methyl esters, the Hyamine phenol red titration is run on the sample before and after the reflux. As already shown in Table 2, this titration is well suited for measuring the increase in carboxylate concentration which results from the saponification.

To determine whether a 30-min reflux period was also sufficient to determine sodium methyl sulfate in an actual finished product, a sample of a sodium alpha sulfo methyl tallowate made in Stepan's pilot plant was accurately weighed into a 250-ml volumetric flask with ethylene glycol. Aliquots of 50 ml were refluxed for

varying lengths of time, along with a blank, and analyzed for sodium methyl sulfate according to the proposed method. The results are given in Table 4.

As further evidence for the accuracy of the method, known amounts of 97% minimum purity potassium methyl sulfate were added to the same pilot plant lot. The resulting mixtures were analyzed according to the new method, with the results given in Table 5. The close agreement between percent added and percent shown in Table 5 is further evidence of the validity of the sodium methyl sulfate determination.

Finally, three separate commercial samples were analyzed for percent oven solids, percent sodium alpha sulfo methyl tallowate, percent disodium alpha sulfo tallow acid, percent free methyl esters, percent free fatty acid, percent sodium soaps, percent sodium sulfate and percent sodium chloride. Percent sodium methyl sulfate was calculated by difference and also determined by the new method. A comparison of the "by difference" and determined results is shown in Table 6. This comparison may be considered good, considering that nine different determinations had to be made to render calculation of the "by difference" result possible.

In addition to the new methods for sulfonates and sodium methyl sulfate already discussed, the procedures used in our laboratories to perform a complete compositional analysis are summarized in Table 7. Using these determinations, the compositional analyses of three commercial products are given in Table 8. The close agreement between mass balances and solids is to be noted.

In the preceding determinations, it was found that solids, total sulfonate active, sodium methyl sulfate, free methyl esters, free fatty acid and unsulfonated soap

TABLE 4

Percent Sodium Methyl Sulfate for Pilot Plant Lot as a Function of Reflux Time

Time (min)	% CH_3OSO_3Na
30	3.26
60	3.25
120	3.15
240	3.28

TABLE 5

Potassium Methyl Sulfate Found in Compared to Percent Added to Pilot Plant Lot

Trial	% CH_3OSO_3K Added	% CH_3OSO_3K Found	% Recovery
1	2.81	2.79	99.3
2	2.76	2.70	97.8
3	5.51	5.53	100.4
4	5.40	5.98	110.7

TABLE 6

Results for CH_3OSO_3Na "By Difference" vs those for the Saponification-HPR (HPRSAP) Method on 3 Commercial Lots

Product	% CH_3SO_4Na	
	By Difference	HPRSAP
A	3.09	3.23
B	7.62	6.50
C	5.27	5.17

TABLE 7

Supplemental Methods for Alpha Sulfo Methyl Tallowate Analysis

Component, %	Methods/Calculation[a]
Free fatty acids (FFA)	(AVPEX) (27.5)
Free methyl esters (FME)	PEX-[(AVPEX) (27.5)]
Unsulfonated soap	PEX at pH3 after PEX of FFA and FME
Sodium sulfate	$BaCl_2$ titration to THQ
Sodium chloride	Potentiometric $AgNO_3$
Methanol	GLC (internal standard:IPA)
Water	Karl Fischer (for less than 10% H_2O)
Water	Xylene distillation (for 10% H_2O or more)
Solids	1 g, 2 hr, 105 C

[a]AVPEX, acid value of petroleum ether extract; PEX, petroleum ether extract; FFA, free fatty acids; FME, free methyl esters; THQ, tetrahydroxyquinone indicator; GLC, gas liquid chromatography.

TABLE 8

Compositional Analyses of Commercial Sodium Alpha Sulfo Methyl Tallowate "As Is"

Commercial Product	Percentage		
Na alpha sulfo methyl tallowate ($RCHSO_3Na\ COOCH_3$	52.99	34.23	81.76
Na alpha sulfo carboxylic acid ($RCHSO_3Na\ COOH$)	1.68	0.70	1.81
Di-Na alpha sulfocarboxylate ($RCHSO_3Na\ COONa$)	0.20	0.54	0.92
Total sulfo active (A + B + C)	54.82	35.47	84.49
Na methyl sulfate (CH_3OSO_3Na)	6.50	3.23	5.17
Na_2SO_4	1.87	1.76	6.20
NaCl	none	0.53	0.18
Free methyl ester (RCH_2COOCH_3)	0.74	0.63	0.95
Free fatty acid (RCH_2COOH)	0.24	0.19	0.32
Unsulfonated soap (RCH_2COONa)	0.32	0.25	0.44
Methanol	none	none	none
Water	34.58	—	2.98
Oven solids	65.62	41.85	97.57
Mass balance (D + E + F + G + H + I + J)	64.49	42.06	97.75
Mass balance/solids (N × 100)/M	98.27	101.3	100.2

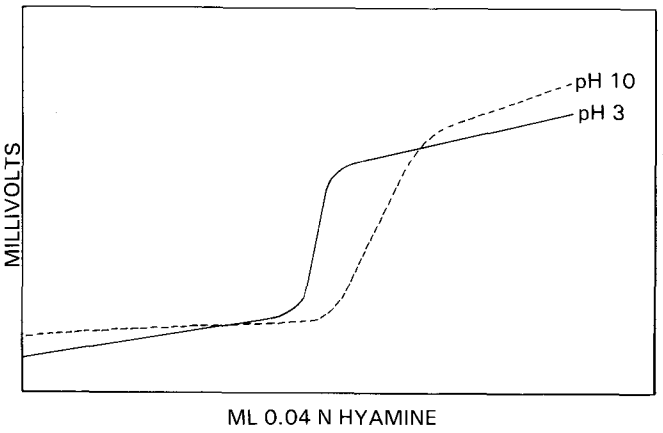


FIG. 3. ISE titration curves, commercial product.

TABLE 9

Comparison of Values for Commercial Samples: Ion Selective Electrode (ISE), pH 3 and pH 10, and Two-Phase Titrations, MB and PR

Me/g			
ISE		2-Phase	
pH 3	pH 10	MB	PR
1.649	1.741	1.651	1.739
1.042	1.096	1.042	1.096
2.170	2.250	2.168	2.252

TABLE 10

Comparison of Values: Wet Chemical vs NMR (0 and 2 hr)[a] for Commercial Samples

Determination	Wet Methods	NMR 0 hr[a]	NMR 2 hr[a]
Sample 1			
Na alpha Sulfo Methyl Tallowate, %	86.33	59.94	42.03
Di Na alpha Sulfo Tallowate, %	0.33	28.78	42.88
Na alpha Sulfo Tallow Acid, %	2.74		
CH_3OSO_3Na, %	10.60	11.28	15.09
Sample 2			
Na alpha Sulfo Methyl Tallowate, %	88.45	86.52	47.45
Di Na alpha Sulfo Tallowate, %	1.40	5.20	39.34
Na alpha Sulfo Tallow Acid, %	1.81		
CH_3OSO_3Na, %	8.35	8.28	13.21
Sample 3			
Na alpha Sulfo Methyl Tallowate, %	91.19	70.99	40.00
Di Na alpha Sulfo Tallowate, %	1.03	18.97	44.91
Na alpha Sulfo Tallow Acid, %	2.02		
CH_3OSO_3Na, %	5.77	10.04	15.08

[a]In 0.5 ml CD_3COOD + 2 drops H_2SO_4 at 80 C.

contents can be determined by an experienced operator within 2.5 hr. For Na_2SO_4, NaCl, and water and methanol if necessary, perhaps another two hr can be added. This makes about 4.5 total for a complete sample analysis.

ION SELECTIVE ELECTRODE AND NMR APPROACHES

While the principal intent of this paper is to demonstrate how alpha sulfo methyl tallowates can be analyzed using ordinary laboratory equipment, titrations using ion selective electrodes (ISE) and the NMR approach of Hashimoto and Nagai (2) also were investigated.

The ion selective electrode titration was based on ASTM Standard Method D 4251 (10), in which an aqueous solution is titrated potentiometrically against 0.04 N Hyamine 1622 solution using a nitrate ion selective electrode and a silver/silver chloride reference electrode. Since both sulfonates and carboxylates are present in this product, it was felt that titration at pH 3 gives sulfonates only, while titration at pH 10 gives the sum of both materials. Thus, titration at pH 3 should yield the same value as the Hyamine-methylene blue titration while titration at pH 10 should yield the same value as Hyamine-phenol red. In Figure 3 typical titration curves for a commercial sample at both pH's is given, while in Table 9 a comparison of ISE and two-phase titration values is given. It is evident that agreement is quite good.

The use of the ISE method instead of two-phase titration in the sodium methyl sulfate determination cited above also gave good results. Once again, drop by drop addition of a small amount of Makon 10 helped solubilize powders and carboxylates.

In the NMR method, the sample is scanned in 0.5 ml of acetic acid-d_4 plus 2 drops of sulfuric acid at 80 C in order to (i) keep it in solution, and (ii) separate the methyl signal of sodium methyl sulfate and the methyl ester signal completely. The results in Table 10 do not show good agreement. It is not known why this is so. It is our finding, however, that this procedure generally gives high carboxylate and methyl sulfate results, while leaving commercial products standing for prolonged periods at very low pH and high heat does result in a decline of alpha sulfo methyl tallowate and increases in disodium alpha sulfo tallowate and sodium methyl sulfate. This indicates that some hydrolysis of the methyl ester is occurring, and is in agreement with the results of Knaggs et al. (9).

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