The True Molecular Weight of Sulfonate Soaps

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Abstract

The true mol wt of a sulfonate soap can be determined by osmometry if the soap is initially converted to its methyl ester. Conversion is effected by reacting the soap with $(CH_3)_2SO_4$ under proper conditions. This method not only affords a simple and reliable means of measuring sulfonate mol wt, but also allows one to characterize a particular sample in terms of its disulfonate and sulfone content.

Introduction

OIL-SOLUBLE SOAPS of high mol wt sulfonic acids have been used commercially for many years. The sulfonic acids are generally prepared by sulfonation with sulfur trioxide or oleum of the naturally occurring alkyl aromatic components of mineral oil or high boiling (>600F) synthetic detergent alkylate. The sulfonation reaction normally produces mono- and disulfonic acids as well as some sulfones. The oil solubility of a particular sulfonate material can be expected to depend, to a large extent, on its average mol wt, as well as its disulfonate and sulfone content. A simple analytical method that would furnish this information would aid those interested in monitoring the product quality of commercial sulfonates.

Experimental

Preparation of Methyl Sulfonates. The various methyl sulfonates examined in this study were prepared in the following manner. Five g sulfonate soap, isolated from diluent mineral oil by dialysis (1–3), 3 g dimethyl sulfate and 5 g $NaHCO_3$ were weighed into a 500-ml, round-bottomed flask. Two hundred ml xylene were added. The mixture was heated at reflux for three hr and stirred with a teflon bar magnetic stirrer. At the end of the reflux period, the reaction mixture was allowed to cool before filtering. The filtrate was placed in a round-bottomed flask and connected to a film evaporator equipped with a water jacketed condenser, two dry ice traps and a vacuum pump. The flask was heated by a hot water bath and the solvents stripped under 1 mm Hg. vacuum for approx two hr. Approx 4.5 g of a clear viscous amber liquid was usually obtained by this procedure.

Molecular Weights by Osmometery. Solutions of 1–5 g methyl ester/1000 g *o*-dichlorobenzene were prepared. The mol wt measurements were obtained on a Mechrolab Model 302 vapor pressure osmometer that had been standardized with samples of *n*-tetracosane and *n*-dotriacontane obtained from the Humphrey-Wilkinson Corp. The overall average reproducibility observed for duplicate samples(averages of five duplicate determinations of different samples) was 7. The range of individual reproducibilities ran from 3–9. Duplicate determinations run over a fourfold concn variation gave essentially equal mol wt.

Equivalent Weight by Sap. Equivalent. ASTM Test Method D-94 (4).

Equivalent Weight by Ion-Exchange. Sulfonate samples (10–70 g) were dissolved in 3–4 times their volume of heptane and slowly passed through a column made up of several hundred g either Amberlite IR-140 or Permutit Q cation exchange resin. The column was washed with excess heptane followed by isopropanol, followed by water. All the washings were combined with the original eluate. The solvents were evaporated on a steam bath under a stream of nitrogen, final traces being removed by heating in a vacuum oven at 80C. The completeness of conversion was checked by a sulfated ash determination on the free sulfonic acid. The neutralization equivalent of this material was determined (5).

Sulfur Analysis. ASTM Test Method D-129 (6).

Discussion and Results

The conversion of a particular sulfonate sample to its corresponding methyl ester affords a convenient means of characterizing the material in terms of its average mol wt as well as disulfonate and sulfone content. The average mol wt of the methyl ester can be obtained directly by osmometric measurements under proper conditions. Previous experience had shown that the apparent mol wt obtained from osmometric measurements on the original soap were too large by at least an order of magnitude. This is because dissolved surfactant molecules tend to cluster in aggregates commonly referred to as micelles. The apparent mol wt under these conditions is that of the total aggregate rather than that of unassociated surfactant molecules. The reduction in polarity attending the conversion of a sulfonate soap to its methyl ester reduces this tendency to associate to a sufficient degree so as to enable one to obtain true mol wt from osmometer measurements. The limited success reported by earlier workers (7) utilizing a similar approach was probably because they were unable to work at dilutions made practical by modern instruments. In this study the concn (molality) employed were one-tenth to one-twentieth of those used by the previous workers. The higher temp (130C as compared to 80 and 110C, respectively) employed in this study would also tend to reduce the trend of surfactant molecules to associate. This is shown by the fact that the apparent mol wt of typical methyl sulfonates did not vary over a fourfold concn change (Table I).

The equivalent or combining wt, based on the sulfonic acid function, can be obtained from the saponification equivalent of the ester. The disulfonate content can be estimated from the difference between the two, i.e., average mol and equivalent wt. The degree of sulfone formation can be estimated from the difference in the observed sulfur content of the ester as determined by direct elemental analysis and that calculated on the basis of the sulfonate equivalent wt.

The methyl esters of six typical materials of commerce were prepared. Ther respective mol wt were determined by osmometry. The results show in Table II.

Two methods were used in determining the equivalent or combining wt of the soap. The equivalent wt of some of the samples were calculated from the saponification equivalents of their methyl esters. The equivalent wt of the rest were obtained by converting the soap to the corresponding free acid on an ion ex-

TABLE I

Apparent Molecular Weight of Methyl Sulfonates
(Osmometer, *O*-dichlorobenzene Solvent, 130C)

Sample	Conc[a]	Apparent *mol wt*	Conc[a]	Apparent mol wt	Conc[a]	Apparent mol wt
1............	1.13	*487*	2.09	*474*	4.02	*483*
2............	1.18	*483*	2.14	*475*	3.91	*486*

[a] G/1000 g solvent.

TABLE II
Characterization of Sulfonates

Sample	Mol wt Osmometry 130C in *o*-dichloro-benzene	Equivalent wt	Sulfur content, %	
			Calc from eq wt	Observed
A	463[a]	453[b]	7.1	7.0
B	546[b]	500[d]	6.4	6.5
C	451[b]	452[c]	7.1	7.1
D	461[b]	452[d]	7.1	7.1
E	479[b]	463[d]	6.9	7.2
F	453[a]	452[c]	7.1	7.1

[a] Prepared from naturally occurring mineral oil aromatics.

[b] Prepared from synthetic heavy detergent alkylate.

[c] Neutralization of free acid + 14 to compensate for contribution of the CH_3 group to the mol wt.

[d] Saponification equivalent.

change column and titrating the resulting free acid with base. Both methods give reliable and reproducible results. The bomb method was used to determine the sulfur content of the methyl esters.

It has been previously mentioned that the presence of disulfonates would manifest itself as a discrepancy between the observed average mol and equivalent wt, respectively. The presence of sulfones would be indicated by a difference in sulfur content calculated from the equivalent wt and that obtained by direct elemental analysis. In five of the samples examined, the equivalent wt were found to be essentially equal to the mol wt, thus indicating negligible disulfonate content. The equivalent wt observed for Sample B, however, was found to differ significantly from its mol wt, the difference indicating a disulfonate content of ~10%. Likewise, the sulfur content estimated from equivalent wt for five of the samples was found to be in excellent agreement with those obtained from direct analysis, thus indicating a negligible sulfone content. In the sixth sample, sample E, a barely significant discrepancy between the two values, was observed.

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Fatty Acid Components of Fried Foods and Fats used for Frying[1]

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Abstract

Oxidation of fat is accelerated at temp as high as those used for frying. The extent of this oxidation has been studied by frying two kinds of foods (chicken or potatoes) in cottonseed oil and in lard. Fat samples, taken prior to use and following 5 and 10 hr of frying (both for chicken and potatoes) were esterified. Subsequent quantitative assays of methyl esters by gas chromatography showed that the linoleic acid content had decreased from 57–49% after cottonseed oil had been used 10 hr for frying. This decrease was present regardless of whether chicken or potatoes were fried. There was no change in the linoleic acid content of lard after chicken was fried, but a decrease from 11.3–5.8% was noted when potatoes were fried for 10 hr.

The fatty acid content of the fat extracted from the potatoes and the fat used to fry them, was the same when sampled at 5 hr. However, at the end of the 10-hr frying period, fat extracted from the potatoes had a lower linoleic acid content than fat used to fry them. Results were the same for both cottonseed oil and lard. Fatty acid components of the fat extracted from the chicken seemed to be affected as much by the fatty acid composition of the chicken itself as by fat used for frying. Whether the chicken was cooked in fat used 5 or 10 hr made little difference.

Introduction

AUTOXIDATION REACTIONS occurring in fats are accelerated at temp as high as those necessary for deep fat frying of foods (1), but the final degradation products differ with the conditions. Studies under controlled laboratory conditions have shown that chemical changes which occur in a fat during heating are dependent on many factors. Some of these factors are: length of time fat is exposed to heat and the temp (2); presence of accelerators of oxidation such as oxygen or oxidation products (3,4); mixed fatty acid composition and the position of the fatty acid in the triglyceride (5); presence of metallic ions such as iron (1); presence or addition of hematin compounds (6); presence of water vapor (4); amt of fat heated/unit of surface area (7); presence of amino acids and carbohydrates (8,9); and processing conditions used to refine, decolorize and deodorize the fat (10).

The possible toxicity and reduced nutritional value of frying oils is still controversial. Some investigators (2,11–14) believe heated fats lose nutritional value and could be a health hazard, but others (15–18) report no toxic polymers present and only slight changes in nutritional value.

Many problems concerning thermal oxidation of edible oils during use are poorly understood and are the subject of extensive research, yet most of the fatty acid data available are based on raw fats. Chang and co-workers (19) found that lard used for frying doughnuts for 50 min showed very little change in fatty acid composition. They also found the linoleic acid content of corn oil used to fry potato chips for 8 hr was decreased from 55–52.2%. Fleischman and co-workers (20) reported that corn oil used 15 min to fry potatoes showed a decrease from 66.5–54.3% in linoleic acid content. They also found the linoleic acid content of cottonseed oil had decreased 65.46–34.80% after chicken had been fried for 2.5 hr. These decreases seem rather large and some error may have been introduced because the data on the oil before use were not obtained from an original sample but an analysis of the same brand of oil before use.

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[1] Journal Paper No. 1130, Mississippi Agricultural Experiment Station.

[2] A portion of the work in this paper is taken from a thesis submitted in partial fulfillment of the requirements for the Master of Science degree at Mississippi State University in January, 1963.