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The Determination of Alkene Sulfonates in Olefin Sulfonates by Ozone Titration

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ABSTRACT

A simple and rapid method is described for the determination of alkene-1-sulfonates in α-olefin sulfonates (AOS). AOS are primarily mixtures (detergent range) of sodium salts of alkene-1-sulfonates (mixture of double bond position isomers) and hydroxyalkane-1-sulfonates plus small amounts of disulfonates in a 30-40% aqueous solution. The analysis consists of titrating the sample in 98% acetic acid-2% water solution with a stream of ozone to an indicator endpoint (Rouge Organol B.S.) which is detected photometrically. In tests with model compounds, a long carbon chain alkene-1-sulfonate, sodium hexadecene-1-sulfonate, and a 1-alkene-1-sulfonate, sodium 1-propene-1-sulfonate, were quantitatively determined with no interference from a hydroxyalkane-1-sulfonate, sodium hydroxytetradecane-1-sulfonate. In contrast, an alternative method of determining unsaturation, Brown hydrogenation, does not quickly and quantitatively determine 1-alkene-1-sulfonates.

INTRODUCTION

Alpha olefin sulfonates (AOS) are produced from linear detergent range alpha olefins by sulfonation followed by hydrolysis (1). Olefin feedstock has originated from two routes: thermal wax cracking and Ziegler polymerization of ethylene. In late 1977 an additional 125 million pounds of detergent range (C_{10}-C_{20}) linear alpha olefins derived from ethylene became available via new oligomerization technology. The higher purity of ethylene-derived olefins make them prime candidates for conversion to AOS and other derivatives. The attractive properties of AOS in the areas of detergency (2) and biodegradability (3) led to a need for simpler and quicker methods for determining specific component types in the AOS product. This paper describes one such method which was developed for the determination of alkene sulfonates, the principal surfactant present in AOS.

Alpha olefin sulfonates are primarily mixtures (C_{12}-C_{18} range) of sodium salts of alkene-1-sulfonates (mixture of double bond position isomers) and hydroxyalkane-1-sulfonates together with small amounts of disulfonates and unreacted material (olefins, secondary alcohols, sulfonate esters and sultones). Principal surfactant or active matter components in AOS are the alkene-1-sulfonates (50-70% of the total) and hydroxyalkane-1-sulfonates, as well as small amounts of disulfonates. Together, these sulfonates comprise 30-40% of the total weight of the aqueous AOS solution.

Three quantitative methods have been used to determine the amount of alkene-1-sulfonates present in AOS. Hydrogenation using a 5% palladium on alumina catalyst has been extensively studied (4). A mixture of sodium 2-hexadecene-1-sulfonate through sodium 5-hexadecene-1-sulfonate (including all isomers in between) was quantitatively determined by this method. However, a mixture of 45% sodium 1-hexadecene-1-sulfonate and 55% sodium 2-hexadecene-1-sulfonate gave only 67% of the theoretical hydrogen uptake, which indicates that most of the 1-hexadecene-1-sulfonate is not being determined by hydrogenation. We have also found that hydrogenation of AOS according to the procedure of Brown and Brown (5) gives results which are low in value. The second quantitative method, a gas chromatographic (GC) one (6), is very complex and lengthy in that water removal, hydrogenation, and sulfurylization of the sample must proceed the GC analysis. The third method involves thin layer chromatography (7) followed by charring with hot SO_3 fumes and measurement of the charred compounds using a scanning photodensitometer. The method is limited by the usual quantitation problems of thin layer chromatography.

In the interest of developing a rapid, simple method for alkene sulfonates which would not have the limitations of the above methods, we have investigated an ozone titration technique (8). This technique was developed at Koninklijke/Shell-Laboratorium, Amsterdam, several years ago as a general method for determining unsaturation and involves titrating the sample in a chloroform solvent to an indicator endpoint (Rouge Organol B.S.) which is detected

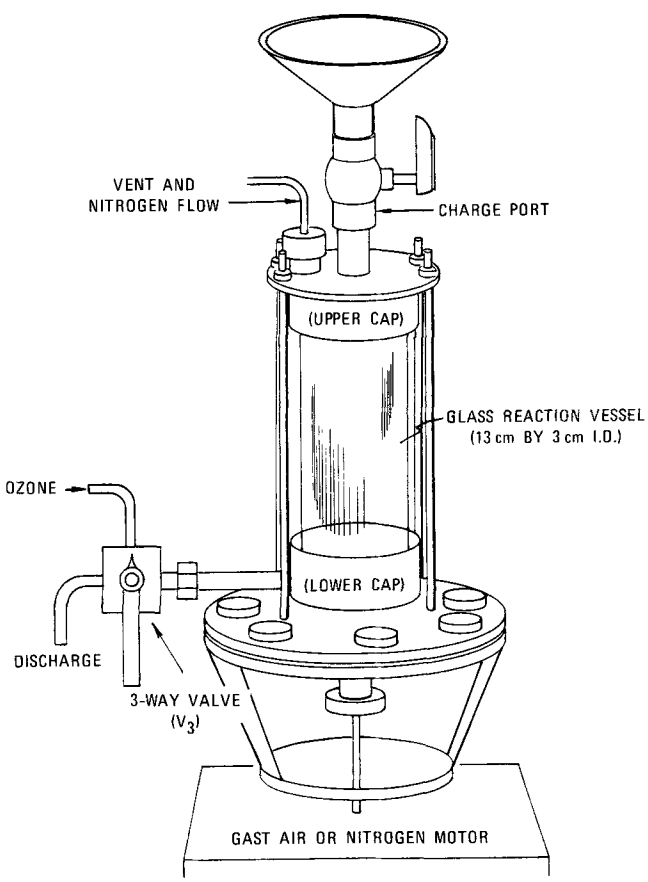

FIG. 1. Reaction vessel.

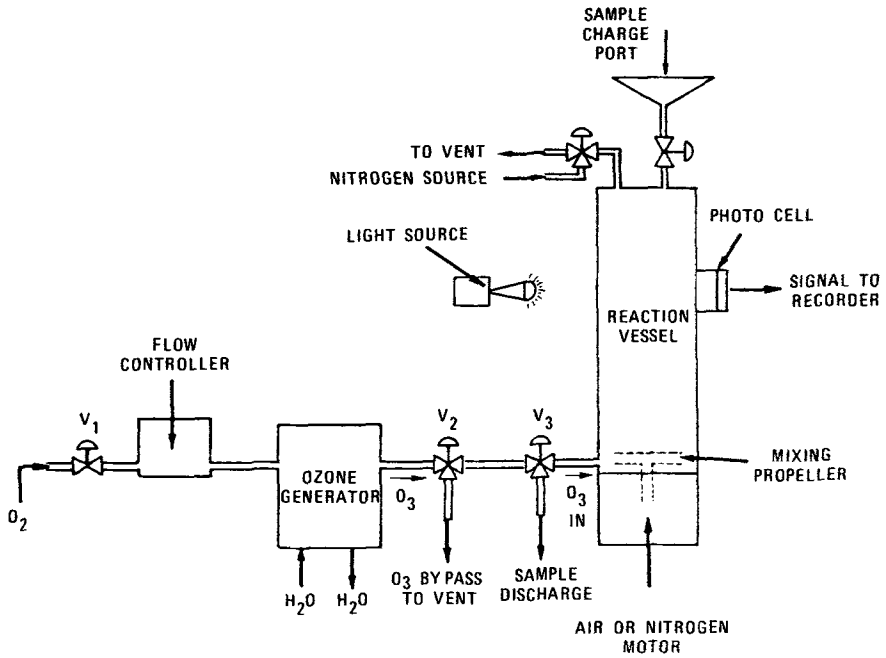

FIG. 2. Ozonolysis titration assembly.

photometrically. Since AOS are not soluble in chloroform, this procedure was not directly applicable. Thus, we have developed an alternative procedure using 2% water in acetic acid as solvent, which permits the rapid and accurate determination of unsaturation in AOS.

EXPERIMENTAL PROCEDURES

Reagents

Sodium hexadecene-1-sulfonate: Prepared in 98% purity by a method similar to that reported in the literature (1,4,7).

Sodium hydroxytetradecane-1-sulfonate: Prepared in 98% purity by a method similar to that reported in the literature (1,4,7).

Sodium 1-propene-1-sulfonate: A crude sample containing 71% sodium 1-propene-1-sulfonate and 12% sodium 2-propene-1-sulfonate was prepared by reaction of sodium 1-hydroxypropane-1-sulfonate with phosphorus pentachloride followed by treatment with sodium carbonate (9).

Rouge Organol B.S. indicator: This indicator is available from Cie Francaise des Matieres Colorantes, 15 Boulevard de l'Amiral-Bruix, Paris (16), France. It is used as a 0.13%w solution in acetic acid.

Olefin calibration standard: 1-Dodecene of 99.9% purity is available from Chemical Samples Company, Columbus, Ohio 43221.

Olefin calibration solution: 1-Dodecene (3.00g.) is weighed to the nearest mg. into a 1 liter volumetric flask and diluted to the mark with 98% acetic acid.

Apparatus

Ozone generator: Model 03V5-0 manufactured by Ozone Research and Euipment Corporation, Phoenix, Arizona 85019. The apparatus must be provided with means for control and measurement of the gas flow and for circulating cooling water through the generator.

Reaction vessel and titration assembly: As shown in Figures 1 and 2, the nitrogen or air driven stirrer mounted through the bottom of the reaction vessel provides good agitation without interfering with the photocell and light source used for endpoint detection and leaves the top of the vessel unblocked for easy sample and solvent introduction.

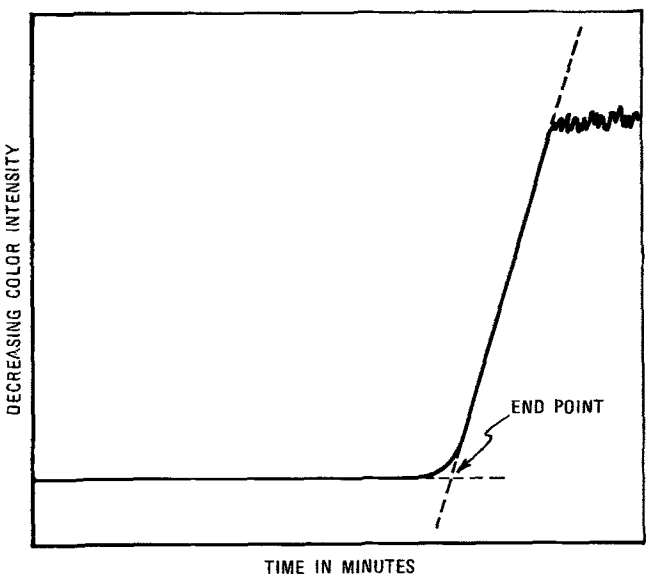

FIG. 3. Chart illustration.

Strip chart recorder: Any recorder with a chart speed of ca. 2.0 cm/minute and a sensitivity suitable for the detector signal is satisfactory.

Photometric endpoint detector: The photometric detector (6) consists of a light source equipped with a 550 nm filter and a light dependent resistor in a Wheatstone bridge circuit with the bridge output connected to the recorder. The reaction vessel is placed in the light path between filter and resistor (Figure 2).

Flask: 500 ml to which a 25 ml automatic pipette dispenser head is attached.

Calibration of the Ozone flow

Ozone is an extremely toxic gas with a threshold limit value of 0.1 ml/m^2. All work should be carried out in a well ventilated hood. With the ozone supply valve V_2 set to by-pass to vent (Figure 2), open the oxygen valve V_1 and adjust the flow to 140 ml/min. After turning on the cooling

water, turn on the ozone generator at a voltage setting high enough to produce about 200 milliamps of current and wait 30-60 min for the current to stabilize. Turn on the light source at the same time the generator is started. Transfer by means of a pipette 50 ml of olefin calibration solution into a 4 oz. bottle with a polyethylene lined cap. Add by pipette 1 ml. of indicator solution to the bottle. Transfer this solution to the reaction vessel using 3 portions (total of 25 ml.) of 98% acetic acid to completely wash the dodecene and the indicator into the reaction chamber.

Turn on the stirrer gas (usually nitrogen) flow and adjust the stirring until the liquid vortex is between 1/8 and 1/4 in. below the surface. After turning on the strip chart recorder, open the reactor valve V_3 so that ozone may be admitted to the reactor. Simultaneously switch the ozone supply valve V_2 to "O_3 in" and start the recorder chart drive. The gas should be completely dispersed throughout the entire solution. If channeling of the ozone through the center occurs, the stirring is too fast and should be reduced. Allow the ozone stream to escape into the fumehood. Continue the ozone titration until the recorder pen rises sharply and then levels out at a higher position (Figure 3). Switch ozone supply valve V_2 to "O_3 by pass" position and turn off the recorder chart drive. Switch the reactor valve V_3 to the "sample discharge" position and collect the product mixture in a flask for disposal. Wash the reaction vessel four times with 25 ml. portions of 98% acetic acid. After the last washing, switch nitrogen flow into the reactor for about 30 sec. Turn the reactor valve V_3 from the "sample discharge" to the "close" position. The reactor is now ready for the next determination. Repeat the calibration procedure with another sample of the dodecene solution. The two calibration samples should agree within 1% of the mean. As some variation in ozone flow is noted, we recommend recalibration with dodecene every 90 min.

Run at least three blanks of 98% acetic acid repeating the procedure described above. Blanks should typically require about 0.5 min titratiom time to reach the endpoint and should agree within 0.02 min.

Analysis of AOS and Other Samples

Weigh into a 4 oz. bottle ca. 1.0g. (to the nearest 0.1 mg) of AOS sample [30-40% active matter (1) in water] and dissolve in 50 ml. of 98% acetic acid. With sodium hexadecene-1-sulfonate and sodium 1-propene-1-sulfonates, the samples' weights are about 0.20 g. and 0.08 g, respectively. With some samples it may be necessary to heat the mixture to 50 C for 10 min to accomplish complete dissolution rapidly. Cool to room temperature before making a determination. Add by pipette 1 ml of indicator solution to each sample solution. Transfer the sample solution to the reaction vessel using 3 portions (total of 25 ml) of 98% acetic acid to completely wash the sample and indicator into the reactor. Repeat the ozone titration procedure with the sample as was described above with the dodecene calibration solution.

Calculations

Calculation of ozone titration time from strip chart recording: Scribe a straight line through the straightest section of the trace that represents the increasing signal (solution color fading from red to pale yellow). The intersection of the scribed line and the extrapolated base line is the end point (see Figure 3). Measure the ozone titration time in min to the nearest 0.03 min. With most samples and the dodecene calibration standards, this time should be between 6 and 15 min.

Ozone calibration: The ozone flow, C, in meq. of double bonds/minute is calulated using the following equation,

$$C = \frac{W_D}{(t_D - t_B) \times 168.2}$$

where W_D is the 1-dodecene weight in mg. (about 150 mg); t_D is the 1-dodecene ozone titration time in min; t_B is the blank ozone titration time in min; and 168.2 is the molecular weight of 1-dodecene. C should be 0.08-0.12 meq./min.

Calculation of sample unsaturation: The ozone number, N, in meq. double bonds/gram of sample is calculated using the following equation,

$$N = \frac{(t_S - t_B) \times C}{W_S}$$

where t_S is the sample ozone titration time in minutes; and W_S is the sample weight in grams.

Calculation of alkene sulfonate content: The alkene sulfonate content can be determined by subtracting the unreacted olefin content (usually very small) in meq/g from the above ozone number. The unreacted olefin content can be determined by extracting a weight portion of the AOS sample with petroleum ether and analyzing the extract by standard GC procedures.

RESULTS AND DISCUSSION

Several solvents were initially considered as potential replacements for chloroform for use in the ozone titration of AOS. These included methanol, 2-methoxyethanol, and dimethylformamide which were quickly eliminated since they all reacted with the ozone and failed to give endpoints. However, acetic acid containing 2% water was found to be ideal for this type of application. In comparing the 98% acetic acid-2% water solvent with chloroform, the ozone number (meq. of double bond per gram) of 1-dodecene was determined in both solvents photometrically using Rouge Organol B.S. indicator. The endpoints in 98% acetic acid were found to be sharper than those observed in chloroform, and the ozone numbers in the two solvents agreed to within 1%. The blanks in 98% acetic acid (0.4-0.5 min. at an ozone flow of 0.1 meq./min) were also consistently lower than in chloroform. The blanks in chloroform vary greatly with the chloroform lot running from 0.6 to 2.8 min. at the same ozone flow. It should be noted that both acetic acid and water have been reported (10) to be more resistant to attack by ozone than chloroform. Indeed, chloroform is known (10) to react with ozone to produce phosgene. The ethanol added to the chloroform as a stabilizer may also react with ozone.

In tests with model compounds the ozone number of 98% pure sodium hexadecene-1-sulfonate was determined in 98% acetic acid to be 2.96 meq/g which is 99% of theory. A sample of sodium hydroxy tetradecane-1-sulfonate consumed no ozone, indicating that hydroxy alkane-1-sulfonates do not interfere ($<$0.01 meq/g) with the determination of sodium alkene-1-sulfonates.

Two commercial samples of 40% active matter AOS in water previously analyzed by Brown hydrogenation in this laboratory were reanalyzed for alkene-1-sulfonates by ozone titration. The sodium alkene-1-sulfonate contents determined by ozone titration (0.72 and 0.83 meq/g) were 7 and 12% higher, respectively, than those determined by hydrogenation. The Brown hydrogenation values are believed to be low because the 1-alkene-1-sulfonates do not hydrogenate as readily as the other alkene-1-sulfonates and are therefore not being determined quantitatively by the Brown Method. Marquis has found (11) that about 9% of the double bonds in sodium hexadecene-1-sulfonate (prepared by sulfonation of 1-hexadecene) are in the 1-position. The double bond was found to be mainly (40%) in the 2- and 3-positions. However, Kuemmel has reported (4) that NMR shows that the amount of the 1-hexadecene-1-sulfonate isomer in sodium hexadecene-1-sulfonate can vary from 10 to 37%. To test if the ozone titration determines the unsaturation in a 1-alkene-1-sulfonate, a crude sample of

sodium 1-propene-1-sulfonate was analysed. The sample had previously been analyzed by NMR as containing 71 mol % sodium 1-propene-1-sulfonate, 12 mol % sodium 2-propene-1 sulfonate, and 17 mol % sodium 2-chloropropane-1-sulfonate. The ozone number was determined to be 5.60 meq/g which is 98% of the unsaturation determined by NMR, indicating that 1-alkene-1-sulfonates can be determined by ozonolysis.

On the basis of this evaluation, we now use the ozone titration to routinely determine the unsaturation in all olefin sulfonates (both alpha and internal). More than 50 samples have now been analyzed by this technique, and no difficulties have been encountered. Duplicate results do not differ from the mean by more than 1% for samples containing 0.50 to 1.50 meq/g of unsaturation. Unsaturation due to the presence of both unreacted olefins and sodium alkene-1-sulfonates is determined by this titration. Since the unreacted olefin content (usually very small) can be simply determined by an extraction-GC method, the alkene-1-sulfonate can be determined by difference.

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