Separation and Quantitation of Alkene and Hydroxy Alkane Sulfonates by Thin Layer Chromatography

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ABSTRACT

In the production of detergent range olefin sulfonates a rapid and relatively simple method for the analysis of compounds produced is desirable. This paper describes a thin layer chromatographic technique for the separation and quantitation of the sodium salts of alkene monosulfonates and disulfonates and hydroxy alkane monosulfonates and disulfonates. The separation is accomplished on tracked, unactivated sulfate-impregnated Silica Gel G layers. Standard equilibrated developing tank conditions are employed in conjunction with a developing solvent of chloroform-methanol-sulfuric acid. Visualization of the compounds is based on their suitability for charring by heat and SO_3 fumes resulting from fuming sulfuric acid which is smeared on the inner sandblasted surface of a charring lid. The charred compounds are quantitated using a scanning photodensitometer. Areas of resultant peaks are calculated and related to composition of the sample.

INTRODUCTION

Utilization of thin layer chromatography (TLC) for the separation and determination of detergent range sulfonates has been reported (1,2). Acid char visualization and subsequent evaluation by scanning densitometry has been established as a useful and reliable means of quantitating TLC-separated components (3-5). Another useful technique is employment of thin layer plates that have been tracked or divided into "subplates" of various widths (5-8). These tracks offer the advantages of allowing a greater number of samples to be applied to each plate and greater control over the subsequent photodensitometry and data handling.

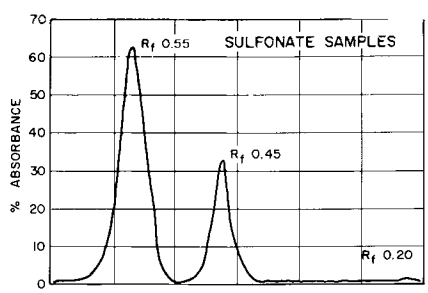

FIG. 1. Photodensitometric trace of typical olefin sulfonate sample.

The development of an analytical TLC method for α-olefin sulfonate products was dependent initially on the availability of standard compounds known to be in the product from hydrolysis of the α-olefin sulfonation product. A number of these standards were synthesized by commonly accepted organic synthesis techniques. Alpha-olefin sulfonate samples may contain alkene monosulfonates, hydroxy alkane monosulfonates, corresponding disulfonates, sodium sulfate, unsulfonated olefin, unhydrolyzed sultones and water. Of these components only the monosulfonates and disulfonates are determined by this thin layer chromatography method. Unhydrolyzed sultones can be determined with some modification of this method.

Application of these various TLC techniques to detergent range sulfonates along with an improved method of char visualization (9) provides a reliable, useful and relatively simple method for the quantitation of these synthetic anionic surfactants. One of the more recently published methods for analysis of α-olefin sulfonates is a gas liquid chromatography (GLC) method by Nagai et al. (10). The GLC method may give somewhat more information, such as isomer distribution, than the TLC method being reported but is far more complex and lengthier in that pre-separation of disulfonates and hydrogenation, sulfurylization and decomposition reactions are necessary prior to separation and determination of α-olefin sulfonate samples.

EXPERIMENTAL PROCEDURES

Sufficient Silica Gel G and 2% aqueous ammonium sulfate (1 g: 2 ml) were slurried and spread on four 20 x 20 cm glass plates of matched thickness. An adjustable mechanical spreader (Desaga/Brinkmann) was used with a gate setting of 250μ to give a uniform layer. The plates were subsequently removed from the spreading board and allowed to dry at ambient temperature overnight in a wooden storage box. Just prior to use they were edge-stripped (1 cm on each side) and tracked (8) (25 tracks, 5

TABLE I

Calibration Standards and Plate Data

Type sulfonate	Amount spotted (μg)	Peak area[a]
Alkene	0.20	5
Monosulfonate	1.00	32
(Sodium-2-tetradecene-1-sulfonate)	2.64	91
	5.18	179
	8.20	243
	12.58	317
OH alkane	0.28	6
Monosulfonate	1.32	45
(Sodium-3-hydroxy hexadecane-1-sulfonate)	3.38	121
	4.78	158
	6.42	200
	7.56	228
	13.18	335

[a]In planimetry units, corrected for track width effect and purity.

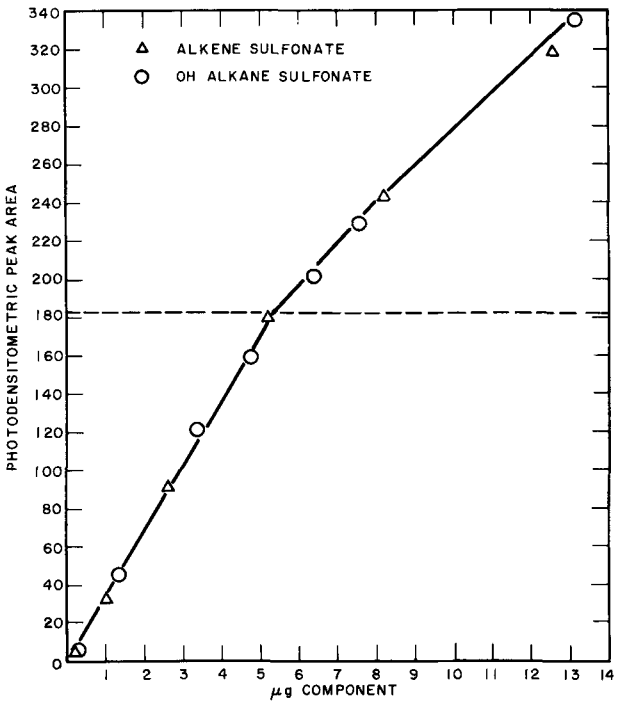

FIG. 2. Calibration curve. △ = alkene sulfonate; ○ = OH alkane sulfonate.

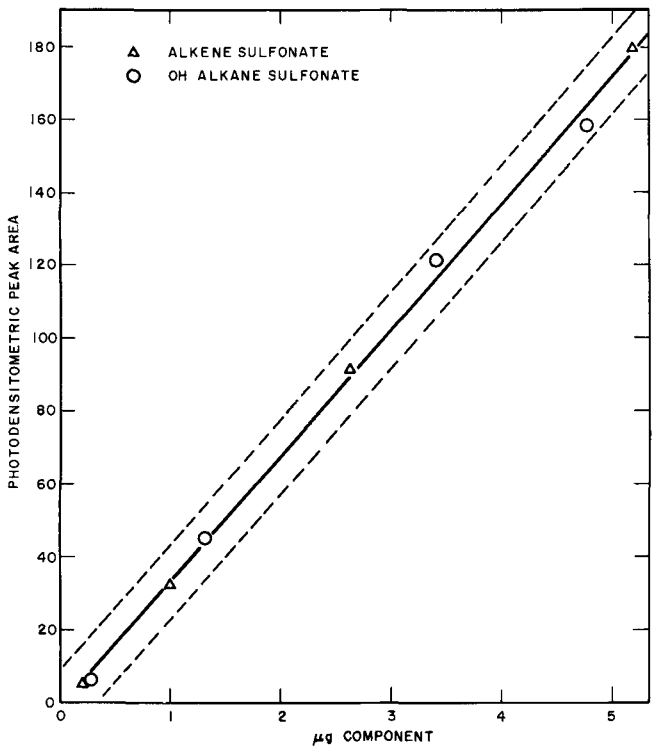

FIG. 3. Calibration curve. △ = alkene sulfonate; ○ = OH alkene sulfonate.

mm track widths).

Two sulfonates, Na-2-tetradecene-1-sulfonate and Na-3-hydroxy hexadecane-1-sulfonate, were selected for primary use due to their higher degrees of purity (95% and 98% respectively). Other standards used on occasion were the sodium salts of 2-hexadecene-1-sulfonate, 2-octadecane-1-sulfonate, 3-hydroxy tetradecane-1-sulfonate and 3-hydroxy octadecane-1-sulfonate. The purity of these compounds was determined by established analytical techniques and checked by TLC. The standards and olefin sulfonate samples from laboratory SO_3 sulfonation of α-olefins were dissolved in a mixture of isopropanol-water (7:3, v/v). Varying concentrations were used for the sulfonate standards. The samples were in a concentration range of 1-5 μg/μl.

In general, alternate tracks on the plate were spotted using 2 μl disposable pipettes at a distance of 2 cm from the bottom edge. After spotting the plates were dried for 15 min in a vacuum oven at 100 C with air bleed (380 mm Hg), removed, cooled to room temperature and placed in a tilted, wick-lined, glass developing tank containing the developing solvent (chloroform-methanol-0.1 N sulfuric acid, 70:32:6, v/v/v). The ground glass edges of the tank and lid were lightly coated with a water soluble grease. The lid was secured to the tank by two stainless steel clamps to ensure vapor equilibration of the tank and plate. After 30 min of equilibration, the tank was righted to start development and developed to the top of the plate (approximately 1 hr). The plate was removed from the tank, dried in a vacuum oven with air bleed at 110 C for 10 min. This time/temperature combination is sufficient for removing the solvent from the layer. The charring technique has been described elsewhere (9) and essentially consists of placing the plate on a block heater and charring with SO_3 fumes resulting from the application of pyrosulfuric acid containing 20-23% SO_3 on the inner sandblasted surface of a char lid. The charring process was completed in 20 min at 150 C.

On completion of the charring cycle the plate was removed from the block heater, the exposed glass areas cleaned of any excess acid which might have collected on the edges of the plate and stored overnight in a wooden, light-tight storage box. A photodensiotometric finish was then applied to the plate.

The densitometry was done on a modified Photovolt instrument with 0.5 x 4.0 mm fixed slit, 2 in./min scan, 4 in./min recorder drive and scanning along the length of the track from solvent front to spot point. The peak areas of the resultant densitometry traces were obtained by planimetry, with baselines drawn tangent to the bottom of the peak.

All organic solvents used were distillation heart cuts of analytical grade reagents, the purity of each checked by TLC.

RESULTS AND DISCUSSION

A photodensitometric trace of a typical olefin sulfonate sample is shown in Figure 1. This trace shows varying amounts of the three main components, alkene monosulfonate, hydroxy alkane monosulfonate and associated disulfonates. R_f values are about 0.55, 0.45 and 0.20 respectively.

Table I gives the standards, concentrations used and corresponding densitometric peak areas corrected for ratio

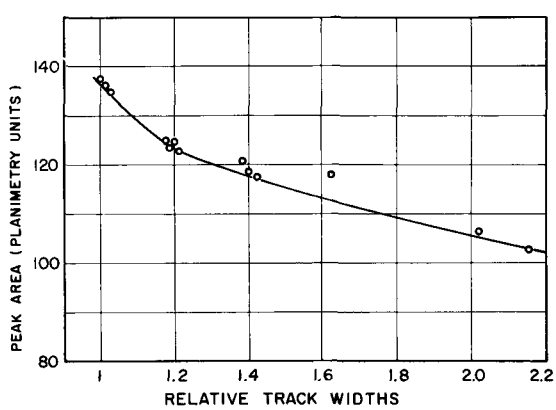

FIG. 4. Track width effect.

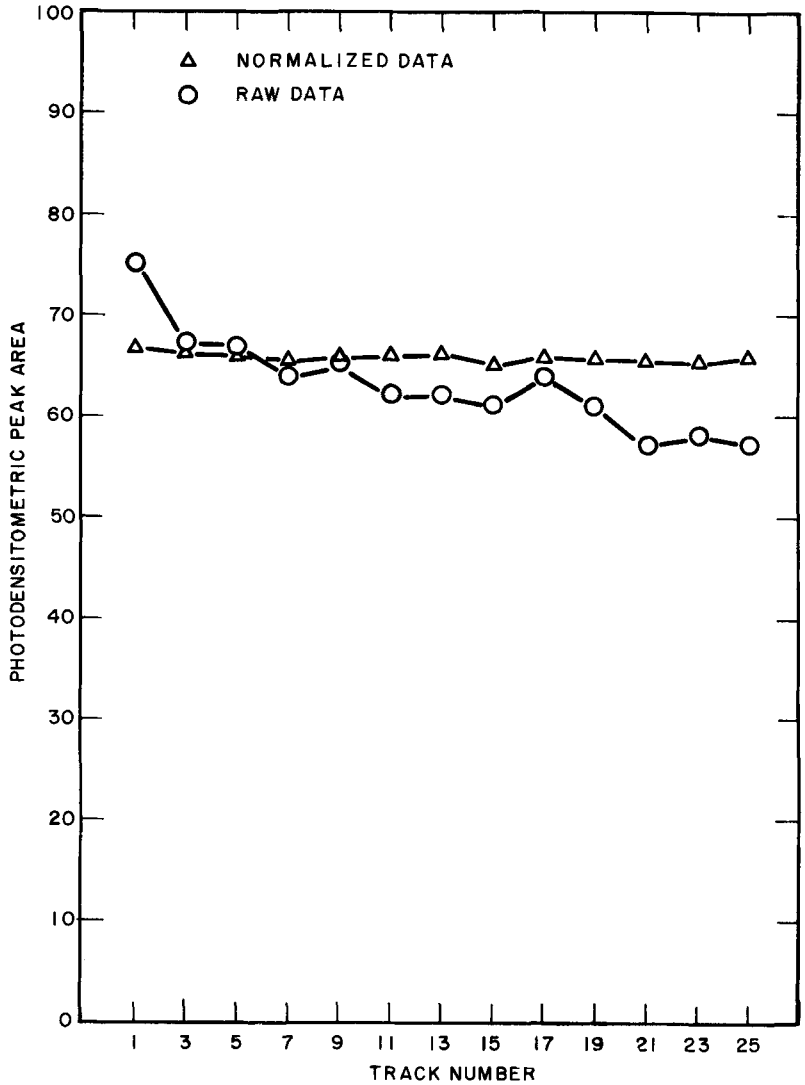

FIG. 5. Temperature gradient effect. ○ = raw data; △ = normalized data.

of per cent carbon and purity. This information is depicted graphically in Figure 2 where the amount in micrograms of components is plotted against the associated peak area.

Photodensitometry is the measurement of the proportion of incident light transmitted by a semiopaque material. At optical densities above 1.3, which correspond to 5% and less transmission, the detection of additional density over the charred zone becomes increasingly less sensitive.

In order to stay within the more sensitive range an optical density of 1.3 is used as the upper limit. This is shown in Figure 2 by the horizontal, dashed line. The optical density of zones corresponding to points below this line is less than 1.3 and greater than 1.3 above the line. This may also be expressed in weight units of practical component loads; i.e., under experimental conditions used, the permissible weight of component per zone is approximately 5 μg. For quantitation the area of most interest is in the range of 0-5 μg of component.

This area of quantitative interest is shown in Figure 3. The data points show a linear relationship between the peak area, corrected for purity and relative per cent carbon and the amount of component. The solid line represents the least-squares line obtained by regression analysis treatment of the data points, while the dashed lines are the 95%

TABLE II

Statistical Treatment, Temperature Gradient Effect Data

	Raw[a]	Normalized[b]	Normalized[b,c]
Number of data points	13	13	13
Mean	63.31	66.08	66.41
Std dev	4.87	0.39	0.52
Var	23.73	0.15	0.27
50% conf limit, rel error	0.94/1.48	0.08/0.11	0.10/0.15
95% conf limit, rel error	2.94/4.65	0.24/0.36	0.31/0.47

[a]Mean in planimetry units.

[b]Mean in percentage.

[c]Plate from different spread.

prediction limits. A correlation coefficient of 0.9988 for these data indicates that the relationship is linear within the stated limits of optical density.

It is concluded from this linearity that olefin sulfonate samples can be determined quantitatively by this thin layer chromatographic technique. The inference of similar charring characteristics or equal carbon yield for these two compounds can be drawn from these data; i.e., differing substituent groups neither appreciably enhance nor impede the carbon yield under the given charring conditions. If the disulfonate compounds have charring characteristics similar to the monosulfonates, subject to the same correction factors and limitations, then a peak area per cent calculation may be made for routine samples, i.e. peak area per cent of A = [(peak area A)/(peak area A + peak area B + peak area C)] x 100. This method of calculation will be referred to subsequently as normalization.

Data normalization simplifies calculations in two major ways: (1) eliminates the necessity for standards in a known system and thereby increases the sample capacity of the TLC plate; and (2) compensates for variations effected by experimental conditions that may be difficult to control in routine operations and thus allows a better comparison of corresponding components track-to-track and plate-to-plate; e.g., if the same sample is spotted on alternate tracks across a thin layer plate, the finished plate data may show minor variations in peak area for corresponding component peaks. The major causes of these variations are small errors in spotting, slightly varying track widths and temperature gradients inherent in the charring block (9). Each of these causes and effect of normalization will be discussed in turn.

Since each track is essentially independent of tracks elsewhere on the plate, each track can be treated as an individual "sub-plate." Assuming uniform sample solution, slight variations in amounts spotted have equal effect on all components in the solution. Similarly, if component zones are reasonably close within an individual track, the effect of any longitudinal temperature gradient is minimized; and if the region of the track that encompasses all the component zones is uniform in width, then the lateral constraint on the component zones is also nearly equal.

However, from track to track across the plate, variations in the lateral constraint and lateral temperature gradient may occur. The lateral constraint effect is illustrated in Figure 4. A TLC plate was scored to give a number of tracks of widths ranging from approximately 4-10 mm in random order across the plate. A standard sample was spotted on tracks of a variety of widths with the same disposable capillary and the separation and visualization carried out as described previously. After scanning each individual track a scan was recorded perpendicular to the normal scanning mode. Relative track widths were then obtained by measuring the width of the peaks at a consistent point.

The "width" effect appears linear in values up to approximately 20% of the normal track width, and the negative slope of the plot implies an inverse relationship between the resultant peak area and the variation in track width. A correction factor for this variance which has been found to be satisfactory is a simple multiplication of the relative track width with the peak area. Normalization by track eliminates the need for this type of correction factor where the components separated do not differ greatly in polarity.

The effect of a lateral temperature gradient is depicted graphically in Figure 5. Track widths were fairly uniform for this particular set of data, i.e. 5 mm ± 2%, and the same sample was spotted on alternate tracks across the plate. The predominant variation is from the lateral temperature gradient of the charring block. It is apparent from the negative slope that less conversion to carbon which remains on the layer occurs across the plate from track 1 to track 25. If this effect is equal or nearly so for all components contained in each track, then normalization will minimize the temperature gradient effect. This is also shown in Figure 5 by the normalized data plot.

TABLE III

Analysis of Routine Samples

Samples	Number of analyses	Per cent of component determined	Relative % error 95% conf
(1)[a]	6	66.4	1.15
I (2)	6	29.2	2.24
(3)	6	4.4	7.17
(1)	6	65.2	0.96
II (2)	6	29.9	2.01
(3)	6	4.9	4.39
(1)	6	69.5	0.90
III (2)	6	27.8	1.16
(3)	6	2.7	8.97

[a]1 = Na alkene sulfonate; 2 = Na hydroxy alkane sulfonate; 3 = disulfonate.

Table II gives a statistical treatment of the raw data and normalized data used in Figure 5. As shown by comparing these two segments, the precision is increased by a factor of 10 by data normalization. The third segment of Table II is similar data using the same sample but a plate from a different spread. Data normalization also minimizes the effect of slight variations in plate conditions from spread to spread.

The analysis and statistical treatment of three differing routine samples are given in Table III. Percentages are peak area percentages and the relative errors obtained are indications of precision and not necessarily accuracy. Absolute measurements depend to a great degree upon the availability and purity of standards for each component type and utilization of proper correction factors which may be necessitated. Lacking individual standards, there are at least two types of calculations which may be made. One is the normalization procedure which has been discussed; another is to choose one sample of the type that is similar in component composition but not necessarily concentration, establish the composition of the "standard sample" and compare all other samples of similar nature to this one. Either of these methods should yield good precision and accuracy, i.e. within 1-10% relative, depending on the concentration of the component(s) of interest.

Analysis of olefin sulfonate samples by thin layer chromatography and associated SO_3 char and photodensitometric techniques is not only versatile and reliable but reasonably rapid. When routine samples are analyzed in groups of 10 to 15, less than one-half man-hour per analysis is required, and subsequent machine handling of data (e.g., electronic integration, computerization) should further decrease the time required to complete an analysis with little loss in precision.

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