Rate of Color Formation in Sulfonation of Dodecylbenzene with Gaseous Sulfur Trioxide

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ABSTRACT

An experimental method has been developed to study the color formation in sulfonation of dodecylbenzene with gaseous sulfur trioxide. The rate of color formation in dodecylbenzene sulfonation, measured as the light absorbance at 420 nm, has been studied under various conditions, and the results have been correlated to a mathematical model.

INTRODUCTION

One of the capacity limiting factors in most sulfur trioxide sulfonation processes for detergent production is the formation of colored products. From a quality point of view, it is desirable to obtain both a high degree of sulfonation and low color, but this specification may be difficult to fulfill without particular conditions. Most articles dealing with sulfonation for detergent production, particularly those concerning sulfonation with sulfur trioxide, often contain subjective comments on the color of the product. In some articles, the color is given as a color-number on a scale defined by a standard method. To date, the most serious attempt to describe the formation of color in the sulfonation of dodecylbenzene has been made by Hoffmann (1). He studied this phenomenon under various sulfonation conditions to identify by-products that may cause the color. He proposed that the color be measured as the absorbance at 420 nm, where there is a maximum which is independent of the degree of sulfonation. The aim of the present article is to study the rate of color formation under various conditions for sulfonation of dodecylbenzene with gaseous sulfur trioxide. The rate of color formation is described by a rate equation to be used in optimization of a sulfonation plant. The optimization will be described in a forthcoming article.

EXPERIMENTAL PROCEDURES

Materials and Equipment

Dodecylbenzene of commercial quality was used (Table I). The sulfonation was carried out in a jacket glass reactor at constant temperature. The liquid phase was pumped continuously through a temperated glass tube into the flow cuvette in the spectrophotometer and back into the reactor

TABLE I

Quality of Linear Dodecylbenzene

Characteristic	
Molecular wt	240-250 g/mole
Bromine number[a]	0.15
Water content (% wt)	0.05
Aniline point[b]	12-15 C
Boiling point initial	280 C
Dry point	310 C
Flash point	125 C
Refractive index n_D^{20}	1.485-1.487

[a]According to American Society for Testing and Materials D1159.

[b]According to American Society for Testing and Materials D1012.

(Fig. 1). The absorbance was recorded during the run. The delay, due to the tube volume, was ca. 2 sec. Liquid sulfur trioxide was pumped by means of a calibrated pump through a teflon tube into an electrically heated oven, where the sulfur trioxide was evaporated and mixed with flow of dry nitrogen at constant temperature. The gas mixture finally was temperated to ca. 50 C and introduced to the reactor by a sparger.

Additional Comments on Spectrophotometric Determination

The color of commercial detergent products usually is measured in 15% by wt ethanol solution in a colorimeter and compared with an American Society for Testing and Materials (ASTM) color scale (ASTM D1209) (2). The absorbance A in this study can be transformed to this scale by multiplying with a constant C. From colorimetric measurements of the product in 15% ethanol solution and standard color measurements, C was determined to be 153.4 with a standard deviation of 11.7.

Procedure

A weighed amount of dodecylbenzene (120-130 g) was added to the reactor. Dry nitrogen was used to purge air and moisture from the system. At the highest rate of sulfonation, only runs above 65 C could be carried out owing to the great heat of reaction. Forty-six runs were carried out at temperatures between 40-85 C and at various absorption rates between 0.16-2.46 mmol SO_3/s. After each run, the absorption of sulfur trioxide was checked by titrimetric determination of acid in the product. The color of the end product was determined separately in 15% by wt ethanol solution in a colorimeter with blue filter.
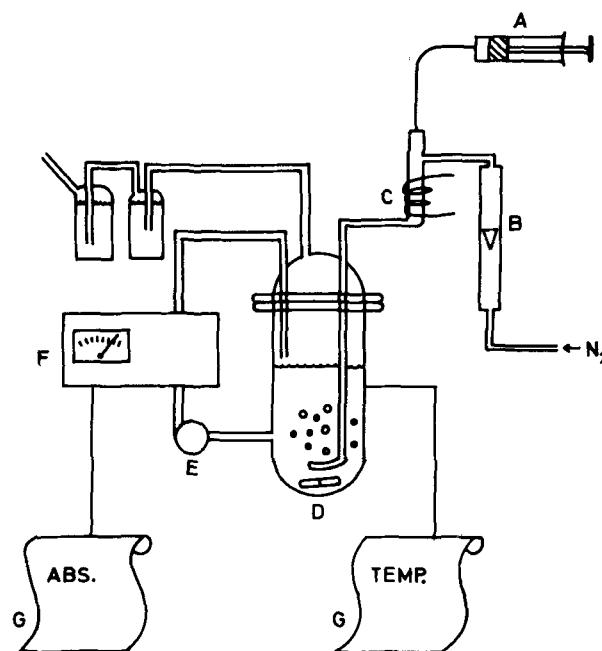

FIG. 1. Experimental apparatus: A = liquid sulfur trioxide pump, B = rotameter, C = electrically heated oven, D = reactor with magnetic stirrer, E = recirculation pump, F = spectrophotometer, and G = recorders.
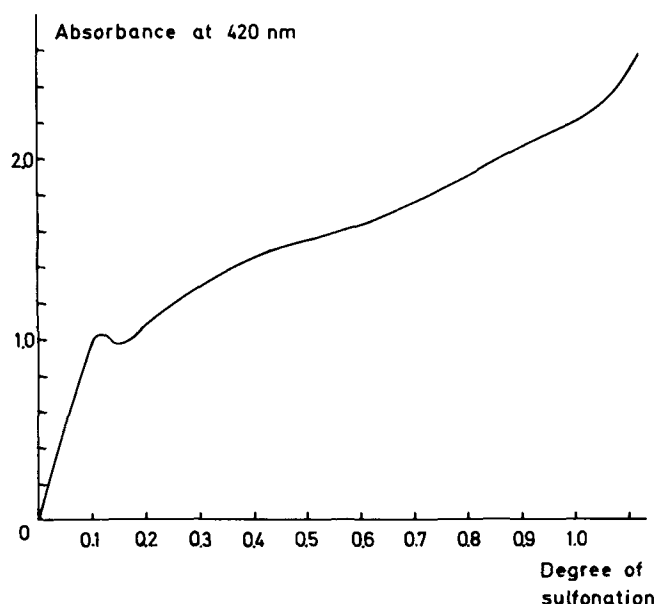
FIG. 2. Absorbance at 420 nm vs sulfonation degree for a typical run. The degree of sulfonation is calculated from the rate of sulfur trioxide addition and the amount of dodecylbenzene in the reactor.

RESULTS AND DISCUSSION

The absorbance vs the sulfonation degree of a typical run is given in Figure 2. In this study, the degree of sulfonation is defined as the moles sulfur trioxide added/ initial moles dodecylbenzene. It is assumed that all sulfur trioxide added reacts with dodecylbenzene instantaneously. Three ranges of the sulfonation process, each with a constant rate of color formation, may be distinguished from the figure. The transition points were found to occur at ca. 0.15 and 0.95 sulfonation degrees in all runs, regardless of the sulfonation conditions. This can be explained by the fact that there are several competitive reactions which form colored by-products. Deviations of ca. 0.03 degree of sulfonation at the transition point occurred due to experimental errors, especially in fast runs. The color formation rates were increased markedly by the temperature and the rate of sulfur trioxide addition. Hoffmann (1) and Haumer (3) found that the sulfonated mixture became darker at increasing temperature. Haumer (3) also found that the color increased with increased partial pressure. The same effect was found in the present study. Obviously, the color is formed mainly during the first part of the run. In the run given in Figure 2, the absorbance at 0.15 degree of sulfonation is about 1.0, which corresponds to 153 units on the ASTM scale. The color limit for an approved product of ca. 1.0 degree of sulfonation is 250 units on the ASTM scale. To avoid a dark product, the sulfonation conditions during the first part of the run are apparently of great importance. Excess of sulfur trioxide also has to be avoided.

On the basis of the present results, it is, of course, impossible to identify the compounds which give rise to the dark color. It should be mentioned that attempts (1) have been made to identify these compounds.

Correlation of Data

It is likely that the rate of absorption is a factor of great importance for color formation. Since the mass transfer coefficient and the contact area are unknown in this study, the absorption rate cannot be calculated by means of the partial pressure. Partial pressure is, consequently, not a good variable for correlation. Instead, the rate of absorption may be calculated from the rate of sulfur trioxide addition, since all sulfur trioxide added was absorbed, as

found by titrimetric determination of acid in the sulfonated liquid. The degree of sulfonation can be calculated from the rate of absorption, since this is constant during each run.

To obtain a simple mathematical model of the color formation, each run was divided into 3 parts, namely, below 0.15, between 0.15 and 0.95, and above 0.95 sulfonation degree. In each part, the rate of color formation was independent of sulfonation degree and could be evaluated from the slope of the straight line. The following exponential model was fitted to the data:

$$(dA/dt) = B(V_{SO_3}/n_0)^\alpha \exp(-E/T),$$

where dA/dt is the rate of absorbance change at 420 nm and B and E are constants to be evaluated. Moreover, V_{SO_3}/n_0 is the feed rate of sulfur trioxide/initial moles n_0 of dodecylbenzene in the reactor.

The model was fitted by linear multiple regression in logarithmic form to each part. For 46, 46, and 37 data points at 0-0.15, 0.15-0.95, and 0.95 sulfonation degrees, respectively, parameter values given in Table II were obtained. The standard deviations were ca. 5% of the value of each parameter. The multiple correlation coefficients were 0.98, 0.99, and 0.94 for each part of sulfonation degree. The poorer correlation in the range above 0.95 is partly due to low accuracy of the absorbance measurements.

Since the color formation is a capacity limiting factor in many sulfonation processes, it is important to have a mathematical description of the formation rate to be able to optimize the process. This article presents a simple experimental method for evaluating a mathematical model for color formation in dodecylbenzene. The proposed model seems to correlate the experimental data well. It must be pointed out that the transition points appeared at different degrees of sulfonation for various batches of dodecylbenzene, and this phenomenon could not be correlated easily to the quality specification. However, an optimization based upon parameter values in this study is probably valid for many types of dodecylbenzene, since the curves are generally similar and the rate of color formation seems to be of the same order of magnitude. For other detergent raw materials, e.g. α-olefin and fatty alcohols, quite different curves were obtained, and, therefore, for these compounds, separate studies must be carried out before an optimization.

REFERENCES

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