

# Determination of Di-(2-ethylhexyl) Sodium Sulfosuccinate and Related Dialkyl Esters in Aqueous Solutions by the Ferric Hydroxamate Procedure

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**Abstract** □ Di-(2-ethylhexyl) sodium sulfosuccinate and its closely related calcium salt, di-(*n*-octyl) isomer, and di-(*n*-hexyl) derivative have shown excellent quantitative response to the ferric hydroxamate reaction under controlled conditions. Their diester structures make them extremely susceptible to attack by the reagent, while hydrolysis is inhibited by the reaction conditions. Optimum conditions for successful determination have been elucidated for the compounds mentioned.

**Keyphrases** □ Surfactant determination—aqueous solutions □ Di-(2-ethylhexyl) sodium sulfosuccinate, related esters—determination □ Ferric hydroxamate procedures—analysis □ Colorimetric analysis—spectrophotometer

The usual methods for analysis of the dialkyl sulfosuccinates (1–6) involve titration of a dye-cationic surfactant complex with the anionic surfactant in aqueous solution in a two-phase system (aqueous buffer solution–chloroform). The inherent problems of foaming, possible emulsification at the interface, and possible incomplete surfactant transfer between the phases are unavoidable disadvantages of these methods. The difficult visual detection of the end-point and standardization of the cationic surfactant present additional problems in the titration techniques. Other proposed assay procedures such as that of Stroehl and Kurzak (7), which requires chloroform extraction of a dye complex formed in an aqueous medium, or those based on reduction of surface tension (8, 9) or production of turbidity (10), or those relying on the Draves test (8) also reveal added difficulties. However, by utilizing the ferric hydroxamate reaction, the assay may be carried out in a single-phase system, with reduced foaming and direct measurement of the formed complex with a suitable spectrophotometer. The problems associated with phase transfer, extraction, possible emulsification, and foaming are eliminated in this procedure.

## EXPERIMENTAL

**Materials**—Di-(2-ethylhexyl) sodium sulfosuccinate, di-(*n*-hexyl) sodium sulfosuccinate, and di-(*n*-octyl) sodium sulfosuccinate were synthesized according to previously recommended procedures (11, 12). Di-(*n*-hexyl) sodium sulfosuccinate and di-(*n*-octyl) sodium sulfosuccinate, which exist as crystalline compounds, unlike di-(2-ethylhexyl) sodium sulfosuccinate which is amorphous (13), were recrystallized from anhydrous methanol (9). Di-(2-ethylhexyl) calcium sulfosuccinate<sup>1</sup> was obtained commercially and decolorized in a methanol solution prior to use.

Reagents were prepared as follows:

1. Hydroxylamine hydrochloride solution (saturated)—dissolve 83 g. of the salt in 100 ml. of water.
2. Potassium hydroxide solution (10.5 *M*)—dissolve 58.8 g. of KOH in a sufficient quantity of water to make 100 ml. of solution.

**Table I**—Absorbance Values Obtained with Reaction at 0°, Room Temperature, and Variable Reaction Times with Samples of Di-(2-ethylhexyl) Sodium Sulfosuccinate

Minutes	0°			Room Temperature	
	Weight of Di-(2-ethylhexyl) Sodium Sulfosuccinate per 5 ml. of Sample Preparation			Weight of Di-(2-ethylhexyl) Sodium Sulfosuccinate per 5 ml. of Sample Preparation	
	1 mg.	2 mg.	3 mg.	2 mg.	3 mg.
0	—	0.059	0.079	0.208	0.327
20	—	0.349	0.473	0.330	0.499
40	—	0.387	0.573	0.305	0.440
60	—	0.408	0.620	0.323	0.456
75	0.235	0.459	0.630	—	—
90	0.202	0.414	0.625	—	—
120	0.209	0.412	0.624	—	—

3. Hydrochloric acid solution—add 100 ml. of concentrated acid to 100 ml. of water.

4. Ferric chloride solution (0.37 *M*)—dissolve 25.004 g. of ferric chloride in a sufficient quantity of 0.1 *N* hydrochloric acid solution to make 250 ml. of solution.

**Instrumentation**—All absorbance readings were obtained on the Bausch and Lomb Spectronic-20 spectrophotometer at 540 nm. with 11.6-mm. (i.d.) cells.

**Procedure**—The procedure followed was an adaptation of the Feldman and Robb (14) method. Various concentrations of samples were prepared from initial aqueous solutions containing 2.5 mg./ml. of surfactant. Samples were brought to a total volume of 5.0 ml. by the addition of water up to a volume of 2.0 ml., followed by the addition of 2.0 ml. of methanol and 1.0 ml. of isopropanol. The samples were then placed in an ice bath to cool. Subsequently, 1.0 ml. of the hydroxylamine hydrochloride solution followed by 1.0 ml. of the potassium hydroxide solution was added to the samples; they were again placed in an ice bath for a period of 1 hr. During this time, white crystals (presumably excess hydroxylamine hydrochloride) formed in the tubes. However, when the samples were brought to room temperature (22–25°), the crystals redissolved. After 1 hr., the solutions were acidified with 2.0 ml. of the hydrochloric acid solution (pH approximately 0.5); transient gas evolution occurred at this point and the crystals gradually redissolved. The solutions were allowed to reach room temperature, and then 1.0 ml. of the ferric chloride solution was added. The solution becomes stable within 1 min.

Since the colored complex fades slightly with time, spectrophotometer readings should be taken immediately at 540 nm. Calculate the amount of surfactant present in the sample, in milligrams, from the formula  $C(A_U/A_S)$ , where  $C$  is the total weight (dry) in milligrams of a suitable reference standard (prepared in aqueous solution such that the final concentration of standard is 1.0–1.5 mg./ml. of solution) treated concurrently with the unknown solution as directed, and  $A_U$  and  $A_S$  are the absorbances obtained for the unknown sample and reference sample, respectively.

## RESULTS AND DISCUSSION

The analysis is composed of two main reaction steps: (a) the possible formation of the dihydroxamic acid, and (b) the formation of a stable red to reddish-brown colored complex of ferric hydroxamate, the intensity of which is proportional to the amount of ester present. Conditions must be controlled so that the base-catalyzed

<sup>1</sup> Surfak, Hoechst.

**Table II**—Absorbance Values Obtained for Related Dialkyl Sulfosuccinates Using the Ferric Hydroxamate Procedure

Total Milligrams Present <sup>a</sup>	Di-(2-ethylhexyl) Sodium Sulfosuccinate	Di-( <i>n</i> -hexyl) Sodium Sulfosuccinate	Di-( <i>n</i> -octyl) Sodium Sulfosuccinate	Di-(2-ethylhexyl) Calcium Sulfosuccinate
0.5	0.130	0.114	0.087	0.128
1.0	0.246	0.274	0.206	0.231
1.5	0.335	0.368	0.283	0.371
2.0	0.536	0.528	0.444	0.462
3.0	—	0.810	0.644	0.703

<sup>a</sup> Per 5 ml. of sample preparation.

hydroxamic acid formation predominates over the alkaline hydrolysis of the ester groups. To suppress hydrolysis and promote hydroxamic acid formation, the reaction is carried out in an ice bath while a high concentration of hydroxylamine is maintained in the mixture.

A hydroalcoholic solution is used to enhance the solubility of the surfactants and prevent turbidity in the solution while maintaining the solubility of the reagents. The ratio of alcohol to water utilized in the procedure was determined experimentally. Initial trials in an all-aqueous medium resulted in turbid solutions at relatively low concentrations (2–3 mg.) of surfactant. However, with the recommended system, samples containing as much as 10 mg. of surfactant produced no turbidity; however, the color density of the solution prevented accurate measurement of absorbance. Substitution of other alcohols (ethanol and *n*-propanol) into the system and adjustment of their ratios revealed no additional advantages.

The effects of temperature on the production of color and length of reaction time were also noted. Results in agreement with Beer's law were obtained with reaction at room temperature (22–25°) as well as at ice bath temperature (0°). However, it was observed (Table I) by varying the length of reaction time that although complex formation is in agreement with Beer's law, it is not directly proportional to reaction time. It is suggested that this variation results from a competitive reaction at room temperature, possibly hydrolysis of the hydroxamic acid at one or both positions as it is being formed. At 0°, this variation is not observed; complex formation increases directly with the length of reaction time (Table I). It may also be observed that according to the greater increase in absorbance between concentrations with the reaction at 0°, greater complex formation occurs at this temperature. For these reasons, the ice bath technique is preferred over reaction at room temperature. Subsequent time trials also showed (Table I) that reaction times slightly longer than 1 hr. might be advantageous; however, this supposition is inconsistent for much longer reaction times.

Absorbance values obtained using this method of analysis for various related anionic surface-active dialkyl esters are shown in Table II. Correlation with Beer's law was observed with concentrations of surfactants up to 5 mg./sample; however, instrument limitations prevented accurate measurement of absorbance near this value. Average molar absorptivities calculated for di-(2-ethylhexyl) sodium sulfosuccinate, di-(*n*-hexyl) sodium sulfosuccinate, di-(*n*-octyl) sodium sulfosuccinate, and di-(2-ethylhexyl) calcium sulfosuccinate are 960, 860, 770, and 1900, respectively. Two precautions which must be taken to achieve absorbance values that conform to Beer's law are: (a) volume measurements in sample dilution must be exact,

and (b) the pH of the solution prior to addition of the ferric chloride must be sufficiently acid.

## CONCLUSION

A satisfactory assay for several of the dialkyl sulfosuccinate anionic surfactants in aqueous solution was developed. The conditions necessary for reproducible reaction have been established. This procedure removes many of the difficulties and disadvantages associated with other methods of analysis for these compounds. The ferric hydroxamate procedure allows simple and accurate determination of these compounds without unnecessarily complex techniques. Additionally it allows for the analysis of low concentrations of these surfactants. It is hoped that the proposed procedure will offer a better and more practical means of analysis than those methods already in use.

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