Separation and Extraction of Φ-Methyl Ester Sulfoxylates: New Features

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ABSTRACT: This paper deals with the separation and purification of Φ-methyl ester sulfoxylates obtained through the sulfoxidation process. Two new steps are implemented during separation of the final product from the nonreacted reagent: (i) hot water is used instead of water/ethanol mixture, and (ii) n-butanol is used as the extractive phase after neutralization instead of ethanol, leading to a product with more than 75% active ingredient. A significant improvement in the separation and purification steps has been obtained. The new procedure allows a complete material balance of the main products formed during sulfoxidation of fatty acid methyl esters and thus can lead to study of the reaction conditions, which can improve both conversion and selectivity.

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KEY WORDS: Extraction, Φ-MES, separation.

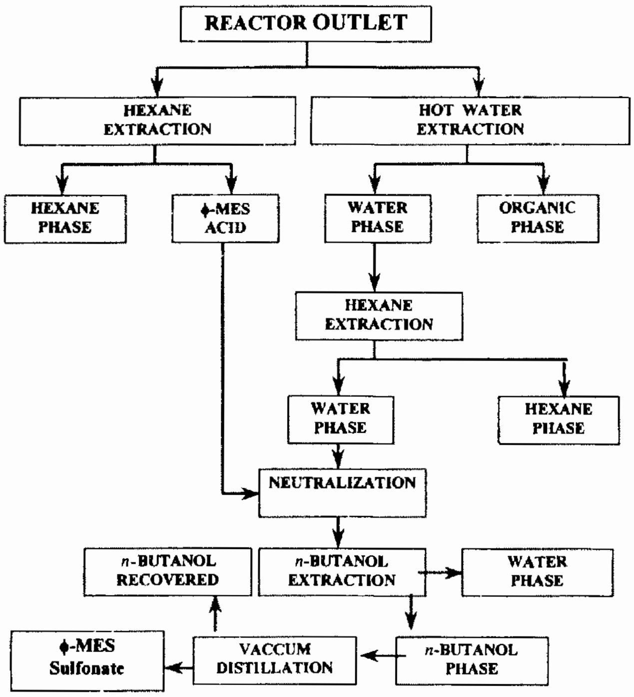
Φ-Ester sulfoxylates (Φ-MES) are new anionic surfactants obtained through sulfoxidation of fatty acid methyl esters with SO_2, O_2, and ultraviolet light of appropriate wavelength. The operating conditions for the synthesis of Φ-MES and the analytical network for its separation and purification have been documented (1). Nevertheless, further work has been performed to improve the separation and extraction processes.

After completion of the sulfoxidation reaction, the reactor product contains mainly mono- and polysulfonic acids; some fatty acids, most probably resulting from fatty methyl ester hydrolysis; some sulfuric acid; and all the nonreacted fatty acid methyl ester since the reaction conversion is close to 30% w/w. It is therefore necessary first to separate the nonreacted methyl ester from the reaction products in order to recover the former for further synthesis. In previous work, the separation procedure proposed has some weaknesses (1). The separation of Φ-MES from the nonreacted methyl ester with a mixture of water/ethanol yields, an organic phase and an acidic phase. However, by this procedure, the separation is incomplete, leaving some impurities in both the acidic and the organic phases. Furthermore, some fatty acid remains in the acid phase, leading to a final product with a significant soap content.

After the separation is carried out, the desired product has to be separated from the unwanted materials such as fatty acid, sulfuric acid and other nonidentified impurities. For purification, the previous method (1) uses ethanol as the extractive phase after neutralization of the acidic phase and dryness. This procedure is time-consuming (several days), and many of the impurities soluble in ethanol are extracted as well, making it impossible to obtain a final Φ-MES product with more than 40% active ingredient. All of these problems have been overcome with the methodology presented herein.

MATERIALS AND METHODS

Separation procedure. The analytical network shown in Scheme 1 depicts two new methods for the separation of the reacted from the nonreacted products, which are mainly Φ-MES sulfonic acid (mono- and polysulfonic acids), fatty acid and nonreacted methyl ester: the hot water extraction method and the hexane extraction method. All of the quantities used in the methods described below are for a C16



SCHEME 1

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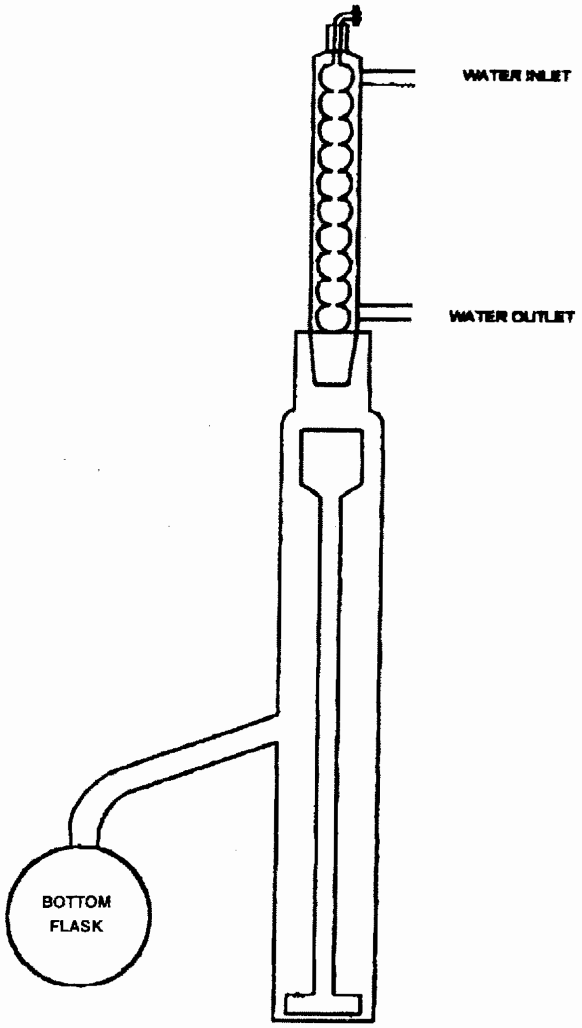

SCHEME 2

methyl ester volume of 250 mL, according to the operating conditions given in Reference 1, and a conversion of 40%.

(i) Hot water extraction: A volume of hot water (250 mL at 60 to 80°C) approximately equivalent to the volume of the reactor outlet is added to the latter in a separatory funnel. The mixture is then shaken and both phases immediately separated. The upper layer (organic phase) contains all of the nonreacted methyl ester and a very small amount of fatty acid, while the aqueous phase (the lower layer) contains all of the sulfonic acid produced and some fatty and sulfuric acids. The fatty acid is then extracted with hexane (100 mL is sufficient for 250 mL of aqueous phase) in a separatory funnel. Finally, the aqueous phase is neutralized with a sodium hydroxide solution (30% w/w).

(ii) Hexane extraction. The reactor outlet is transferred to a liquid–liquid extractor as shown in Scheme 2. The extractor is connected to a round-bottomed flask filled with 600 mL of hexane with the upper part connected to a water condenser. The bottom flask is heated to reflux for 6 to 8 h. The Φ-MES sulfonic acid remains in the extractor whereas the nonreacted methyl ester and fatty acid are recovered in the hexane bottom flask. The acid is then neutralized with a 30% sodium hydroxide solution. This method has the advantage of being water-free.

Extraction procedure. As mentioned previoiusly (2), if the sample dissolves readily in water, extraction from neutral solution with *n*-butanol (the lightest of the homologous series of alcohols to be regarded as immiscible with water) will quantitatively remove most surfactants.

The aqueous Φ-MES neutralized solution is transferred to a liquid–liquid extractor like the one in Scheme 2. In this case, the bottom flask is filled with 600 mL of *n*-butanol. The bottom flask is heated to reflux for 8 h. The Φ-MES sodium salt is recovered in the *n*-butanol bottom flask. The impurities remain in the aqueous phase. The *n*-butanol phase is then distilled under vacuum in a rotary evaporator. *n*-Butanol is recovered for further use, while purified Φ-MES sodium salt is titrated with Hyamine, giving more than 75% active ingredient.

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