

**ANALYSIS OF METHYL ESTER SULFONATION USING  
DENSITY FUNCTIONAL THEORY  
AT B3 LYP/6-31G(D) LEVEL**

**ANÁLISIS DE SULFONACION DEL ESTER METILICO  
USANDO LA TEORÍA FUNCIONAL DE LA DENSIDAD  
EN B3 LYP/6-31G (D) NIVEL**

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**ABSTRACT**

*A mechanism for the sulfonation of methyl esters with sulfur trioxide is proposed herein. Reactions were studied in a falling film reactor and stability of the intermediate species verified by Density Functional Theory calculations at the B3LYP/6-31G(d) level. Mechanistic suppositions and experimental facts asserted a second order kinetic.*

**Key words:** *sulfonation, sulfur trioxide, methyl ester, modeling, density functional.*

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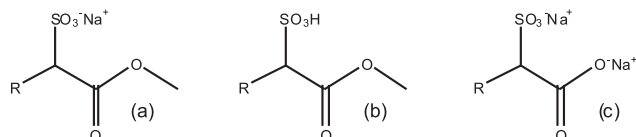
**INTRODUCTION**

Methyl ester sulfonates are anionic surfactants derived from saturated fatty acid methyl esters (ME). In this research ME and SO<sub>3</sub> were obtained from hydrogenated palm oil and fuming sulfuric acid, respectively [Torres et al., 2009]; N<sub>2</sub> was used as a carrier for SO<sub>3</sub>. ME are chemically composed by fatty carboxylates sulfonated at the position alfa respect to the carbonyl group, an alkyl group and typically an organic or inorganic cation bounded to the sulfonic group. Generally these compounds can be represented by the formulas shown in Scheme 1.

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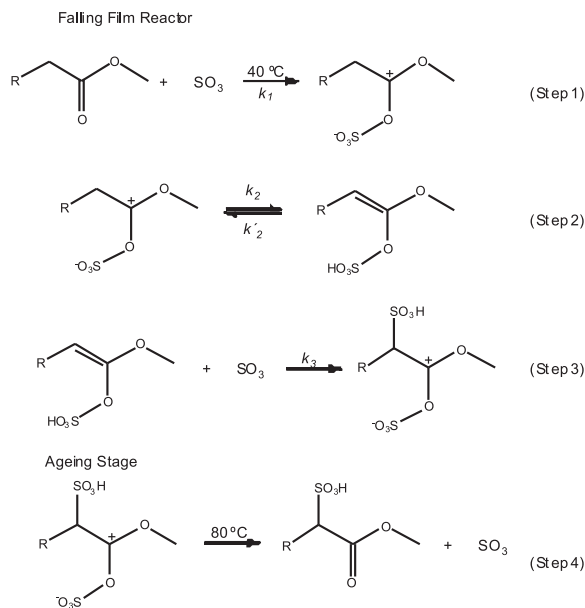
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**Scheme 1.** Methyl ester sulfonates forms: (a) monosodium  $\alpha$ -sulfomethyl ester; (b)  $\alpha$ -sulfonated fatty acid ester; (c) di-sodium  $\alpha$ -sulfo ester (di-salt). R represents a C16, C17 or C18 alkyl substituent.

## METHODOLOGY

The methyl ester sulfonation (MES) chemistry includes both absorption and chemisorption phenomena. Thermodynamic stable structures in the methyl ester sulfonation were calculated using density functional theory at the B3LYP/6-31G(d) level [Cramer, 2002]. Geometry and frequency calculations were carried out using Gaussian 03W [Frisch et al., 2004].



**Scheme 2.** Proposed mechanism to MES in a falling film reactor

The initial reaction steps in the methyl ester sulfonation occur during the ME/SO<sub>3</sub> contact; scheme 2 represents mechanistic facts about SO<sub>3</sub>-sulfonation inside a falling film reactor (FFR). In this mechanism the SO<sub>3</sub> is absorbed by the ME (in liquid phase) originating the intermediate structure RCH<sub>2</sub>COOSO<sub>3</sub>CH<sub>3</sub>. This unstable structure generates another intermediate, RCH(SO<sub>3</sub>H)COOCH<sub>3</sub> (step 2), by activation of its carbon atom in the alpha position. The third step is driven by the reaction of sulfur trioxide with the intermediate RCH(SO<sub>3</sub>H)COOCH<sub>3</sub> generating an over sulfonation thus obtaining RCH(SO<sub>3</sub>H)COOSO<sub>3</sub>CH<sub>3</sub>. This third step is

considerably slower than the previous one. An additional step is necessary for releasing the  $\text{SO}_3$  group which is especially active and therefore able to directly sulfonate another methyl ester molecule. An ageing stage in a batch reactor allowed intermediate decomposition into methyl ester monosulfonated acid and  $\text{SO}_3$  (Scheme 2, step 4).

Experimental evidences [Roberts, 1998] show that the intermediate formation process for methyl disulfonic esters is fast and highly exothermic (150 – 170 kJ/mol, including ca. 25 kJ/mol for  $\text{SO}_3$  heat of absorption). This exothermicity agrees with the results obtained at the B3LYP/6-31G(d) level (Fig. 1). A kinetic study for the ageing stage has been reported elsewhere [Roberts, 2001].

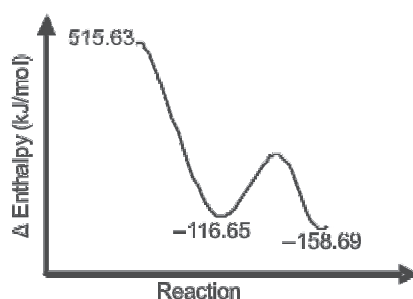


Fig. 1. Enthalpy diagram of the initial reactions of methyl ester sulfonation calculated at the B3LYP/6-31G(d) level.

Due to the presence of aliphatic chains MES is relatively slow compared to sulfonation reaction rates for  $\alpha$ -olefins, alkyl benzenes, ethoxylated alcohols and primary alcohols. Thus, MES could be classified as fast but not instantaneous [de Grott, 1991].

$\text{SO}_3$ -sulfonation of methyl ester has a reaction profile similar to that shown in Fig. 2 for which the third barrier is the controlling step for the total change.

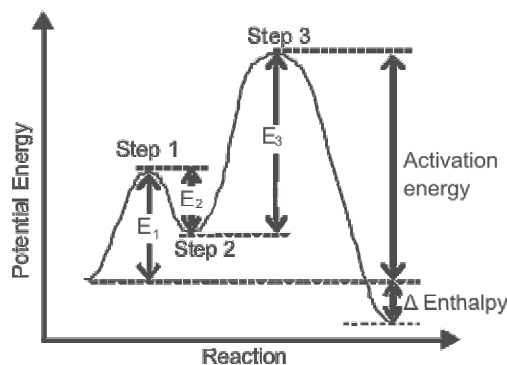


Fig. 2. Potential energy surface in which the third step is controlling the reaction rate

According to the quasi-steady state assumption, the intermediate product is consumed as fast as it is generated and therefore the kinetic for MES can be expressed as:

$$r_{\text{step3}} = k_3 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} C_{\text{SO}_3} \quad (1)$$

Concentration of the intermediary produced in the second step  $C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3}$  can be expressed as follows:

$$r_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} = k_2 C_{\text{RCH}_2\text{COOS}_3\text{CH}_3} - k'_2 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} \quad (2)$$

$$\text{The rate for intermediary } \text{RCH}(\text{SO}_3\text{H})\text{COOSO}_3\text{CH}_3 \text{ is } k_3 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} C_{\text{SO}_3} \quad (3)$$

$$\text{Rate of reaction for intermediary } \text{RCH}_2\text{COOSO}_3\text{CH}_3 \text{ can be expressed as } k_1 C_{\text{ME}} C_{\text{SO}_3} \quad (4)$$

$$\text{Rate of consumption of intermediary } \text{RCH}_2\text{COOSO}_3\text{CH}_3 = k_2 C_{\text{RCH}_2\text{COOSO}_3\text{CH}_3} - k'_2 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} \quad (5)$$

The sum of the preceding rates generates:

$$k_2 C_{\text{RCH}_2\text{COOS}_3\text{CH}_3} - k'_2 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} = k_3 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} C_{\text{SO}_3} \quad (6)$$

$$k_1 C_{\text{ME}} C_{\text{SO}_3} = k_2 C_{\text{RCH}_2\text{COOS}_3\text{CH}_3} - k'_2 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} \quad (7)$$

$$\text{Thus, } k_1 C_{\text{ME}} C_{\text{SO}_3} = k_3 C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} C_{\text{SO}_3} \quad (8)$$

$$\text{Then, } C_{\text{RCH}(\text{SO}_3\text{H})\text{COOCH}_3} = \frac{k_1}{k_3} C_{\text{ME}} \quad (9)$$

Substituting this value of concentration in equation 1 results:

$$\text{Rate of reaction third step} = k_3 \left( \frac{k_1}{k_3} C_{\text{ME}} \right) C_{\text{SO}_3} = k_1 C_{\text{ME}} C_{\text{SO}_3} \quad (10)$$

According to the above, it was searched an equivalent expression for the MES reaction rate. For the especial case where  $C_{\text{SO}_3}$  is high, as in MES [Torres et al., 2008], the reaction in the liquid phase becomes pseudo-first order. This case implies that the reaction is taken place at the gas-liquid interface and therefore, the liquid phase resistance controls the reaction rate. Then the MES reaction rate can be expressed as:

$$\text{Rate} = k_1 C_{\text{SO}_3} C_{\text{ME}} = (k_1 C_{\text{SO}_3}) C_{\text{ME}} = k' C_{\text{ME}} \quad (11)$$

where  $k'$  represents kinetic constant and must be found experimentally.

## RESULTS

Equation 11 is consistent with the reaction scheme (scheme 2) since monosulfonate is delivered from the reaction. Activation energy ( $E_a$ ) was calculated from experimentation as follows in eq. 12 and 13 and in Figure 3:

$$k = Ae^{\frac{-E_a}{RT}} \quad (12)$$

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A \quad (13)$$

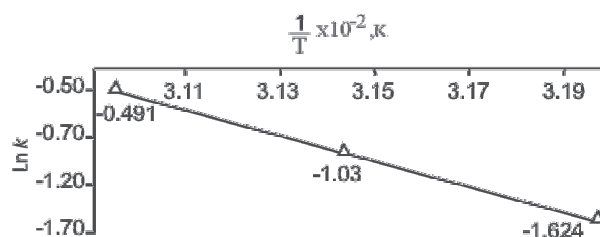


Fig. 3. Effect of the temperature in the MES reaction constant  $k$

Then, the MES activation energy was calculated as 7250 cal/mol which was found to be in the same order than the activation energy for sulfonation of others species [Gilbert, 1965]. Therefore, the kinetics of the methyl ester sulfonation in a falling film reactor was determined as [Torres et al., 2008]:

$$\text{Rate} = kC_{ME} C_{SO_3}, \quad k = 1.14 \times 10^{19} e^{-(14350/T)} \quad (\text{m}^3/\text{kmols})^{-1} \quad (14)$$

This rate allowed computational modeling of the methyl ester sulfonation in a falling film reactor [Torres et al., 2009].

The third intermediate is highly stable according to its predicted Gibbs energy (Figure 4) and the spontaneity of the reaction is favored due to the enthalpy change (Figure 2).

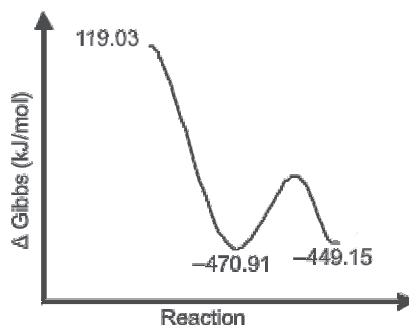
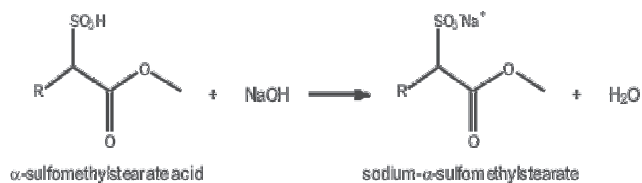


Fig. 4. Gibbs energy profile for the MES calculated using density functional theory at B3LYP/6-31G(d) level

As a matter of information, sulfonation should include a final neutralization stage; this is usually carried out with sodium but it can be done using other monovalent metal ion such as potassium. If neutralization is done quickly (without ageing) the disodium salt is formed otherwise the desired final product sodium  $\alpha$ -sulfomethyl ester is obtained (Scheme 4).



**Scheme 4.** Delayed neutralization

Neutralization process should be designed to minimize formation of both di-salts and intensive coloration. The final sulfonation product consists of a mixture of MES and di-salt, in proportions of ca. 80:20. Sodium methyl sulfate, MeOSO<sub>3</sub>Na, is also present, approximately equal molar with the di-salt [Roberts *et al.*, 2008].

## CONCLUSION

Methyl ester sulfonation mechanism can be classified as an electrophilic addition. It was in agreement with calculations at the B3LYP/6-31G(d) level which showed that intermediate compounds were equally stable. Intermediate molecule needed a final rearrangement step for further stabilization (ageing). Experimental results showed that concentration of methyl ester mono-sulfonated was increased during the digestion stage.

## ACKNOWLEDGMENT

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