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Analysis and identification of minor products in linear alkylbenzene sulphonation

Free-oil extracted in each stage of an industrial linear alkylbenzene (LAB) sulphonation plant was analyzed by HPLC. The identification of its components, mainly unsulphonated LAB, sulphones and anhydrides was achieved by IR and LC-MS. These analyses allow to complete a mass balance in each sulphonation step.

Proben von Freiöl aus jeder Stufe einer industriellen Linearalkylbenzol-(LAB-)Sulfonierungsanlage wurden mittels HPLC untersucht. Die Identifizierung der einzelnen Komponenten, hauptsächlich nicht sulfoniertes LAB, Sulfone und Anhydride erfolgte mittels IR und LC-MS. Diese Analysen erlauben einen vollständigen Massenausgleich auf jeder Stufe der Sulfonierung.

1 Introduction

The reaction section of modern industrial sulphonation plants consists of a film reactor, where sulphuric anhydride reacts with the organic feed, followed by a digestor and an hydrolyzer where the reaction is brought to completion (Scheme 1).

According to the literature [1, 2], the main by-products of linear alkylbenzene (LAB) sulphonation reaction should be anhydrides and sulphones (Scheme 2).

The present investigation deals with free oil extraction after digestion and hydrolysis steps respectively and subsequent analysis by HPLC, LC-MS and IR. The identification and quantification of the mentioned compounds allow to carry out a mass balance of each sulphonation stage and to study how some operating parameters influence reaction conversion and selectivity. The results described here have never been reported elsewhere.

2 Analytical methods and materials

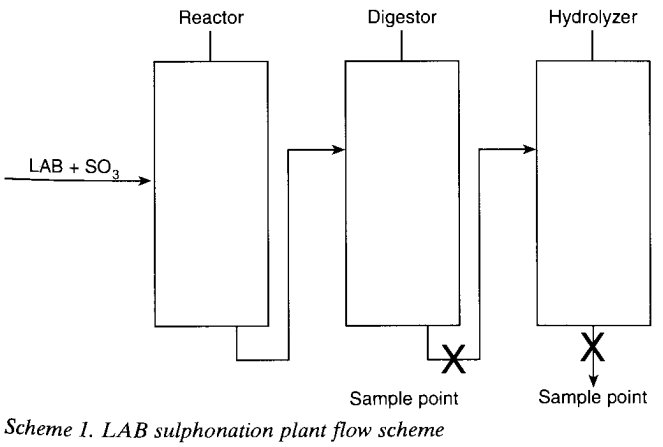
2.1 Free oil extraction

10 g of sulphonic acid are dissolved in 100 ml of an alcohol(ethanol)/water mixture (1/1), then the solution is neutralized with sodium hydroxide. Three extractions with 50 ml hexane are carried out. Finally, hexane is evaporated and the residue is weighted.

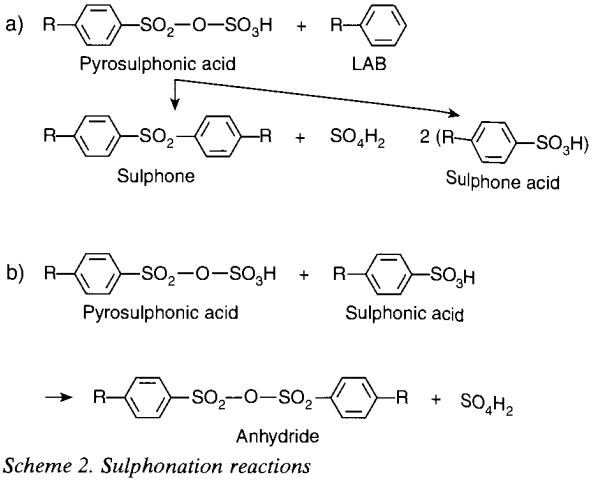
2.2 HPLC analysis

The free oil is dissolved in hexane and the HPLC analysis is then carried out under the following conditions:

HPLC chromatograph:	HP 1090
Column:	Hypersil C8, 5 microns, 200 × 4 mm
Detector:	UV
Solvents:	A: Water/Metanol 75/25 B: Acetonitrile
Flow:	1 ml/min
Gradient:	80 % B initial 85 % B at 5 min 90 % B at 15 min
Volume:	10 microliters



Scheme 1. LAB sulphonation plant flow scheme



Scheme 2. Sulphonation reactions

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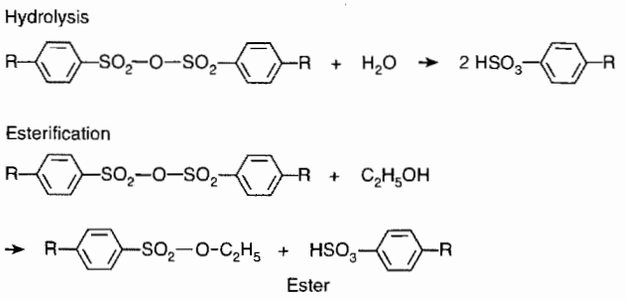


Scheme 3. Reactions of anhydrides

2.3 Materials

Digestor and hydrolyzer outlets were analyzed during the production of Petresul 550. (the reason to eliminate the analysis of the reactor outlet is the unstability of the sample which becomes similar to the digestor with time). The sulphonation conditions are as follows:

Sulphonation plant:	Mazzoni S. A.
SO_3/LAB molar ratio:	1.02
Reaction temperature:	45 °C
Ageing temperature:	48 °C

LAB composition wt %: phenyl C10, 7.3 wt %; phenyl C11, 37.5 wt %; phenyl C12, 33.3 wt %; phenyl C13, 21.9 wt %.

3 Results and discussion

3.1 Analysis and identification of anhydrides

According to the structure of the anhydrides and to the current free oil extraction procedure, two competitive reactions of the formers should take place: Hydrolysis and Esterification (Scheme 3).

Depending on both reaction rates, more or less esterified anhydrides (esters) should appear in the free oil before hydrolysis.

3.1.1 HPLC analysis

At the digestor outlet, before hydrolysis (Fig. 1), four peaks appear before non sulphonated LAB and sulphones, that seem to correspond to C10, C11, C12 and C13 esterified anhydrides. At 210 nm wavelength, phenyl C10 LAB is overlapped by ester C13. However the analysis carried out at 230 nm (Fig. 2), where LAB has no absorption, shows only the four peaks corresponding to the four ester homologues C10 to C13 and the seven peaks of sulphones.

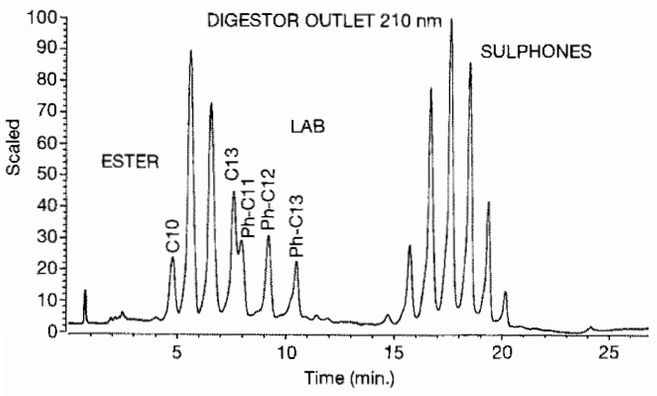


Fig. 1. HPL-Chromatogram of a sample taken from the digestor outlet with UV detection at 210 nm

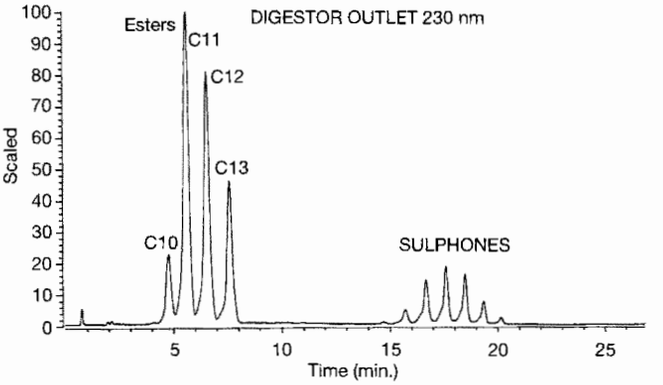


Fig. 2. HPL-Chromatogram of a sample taken from the digestor outlet with UV detection at 230 nm

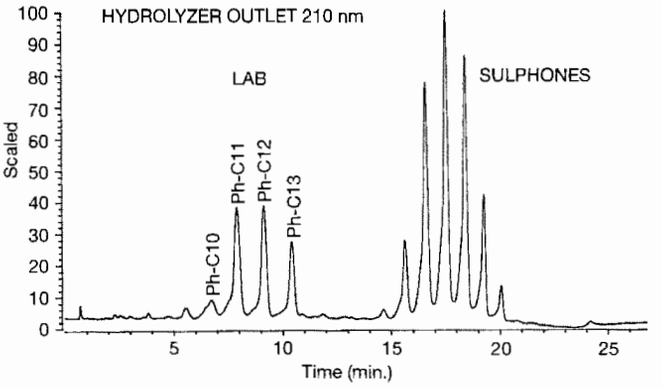


Fig. 3. HPL-Chromatogram of a sample taken from the hydrolyzer outlet with UV detection at 210 nm

At the hydrolyzer outlet (Fig. 3), anhydrides have been hydrolyzed and esters are no more present, therefore free oil is only composed by LAB and sulphones.

3.1.2 LC-MS analysis

In order to confirm the above hypothesis, two free oil samples taken before hydrolysis were analyzed by LC-MS: one extracted with an ethanol/water solution and another one extracted with an isopropanol/water solution, by this way ethyl and isopropyl esters should be formed. Fig. 4 shows the LC-MS spectra for ethylester C11 (molecular weight 340) while Fig. 5 shows the C11 isopropylester (molecular weight 354). C10, C12 and C13 were also identified, thus confirming anhydride structure. Because of its low concentration LAB is not detected by the MS detector.

3.1.3 IR spectra

Free oil before and after hydrolysis was analyzed by infrared spectroscopy. Four peaks appear on the IR spectra corresponding to the sample containing the esters that are absent in the hydrolyzed sample as shown on Fig. 6 and 7. The first two peaks at 1178 and 1190 cm^{-1} should correspond to the vibrations of the S–O_2–O group and the other two peaks at 919 and 1008 cm^{-1} should belong to S–O–R vibrations.

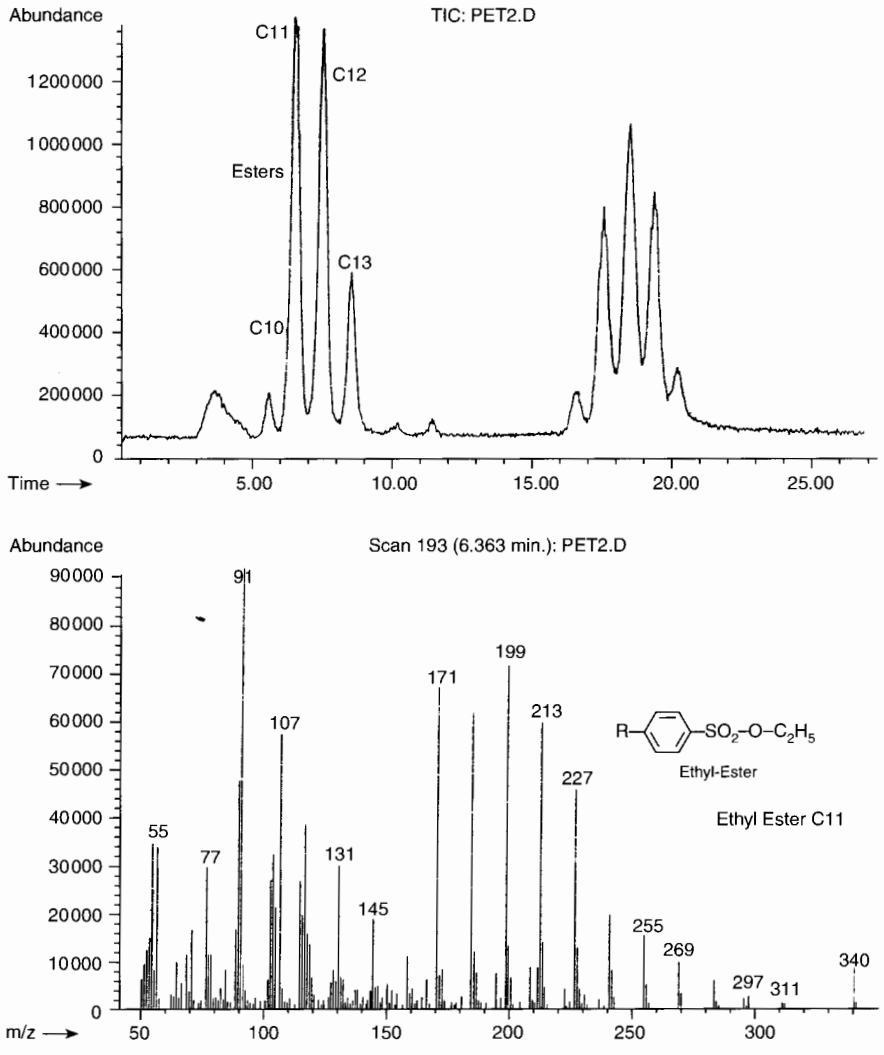


Fig. 4. LC-MS-spectrum of a free oil sample extracted before hydrolysis with ethanol/water

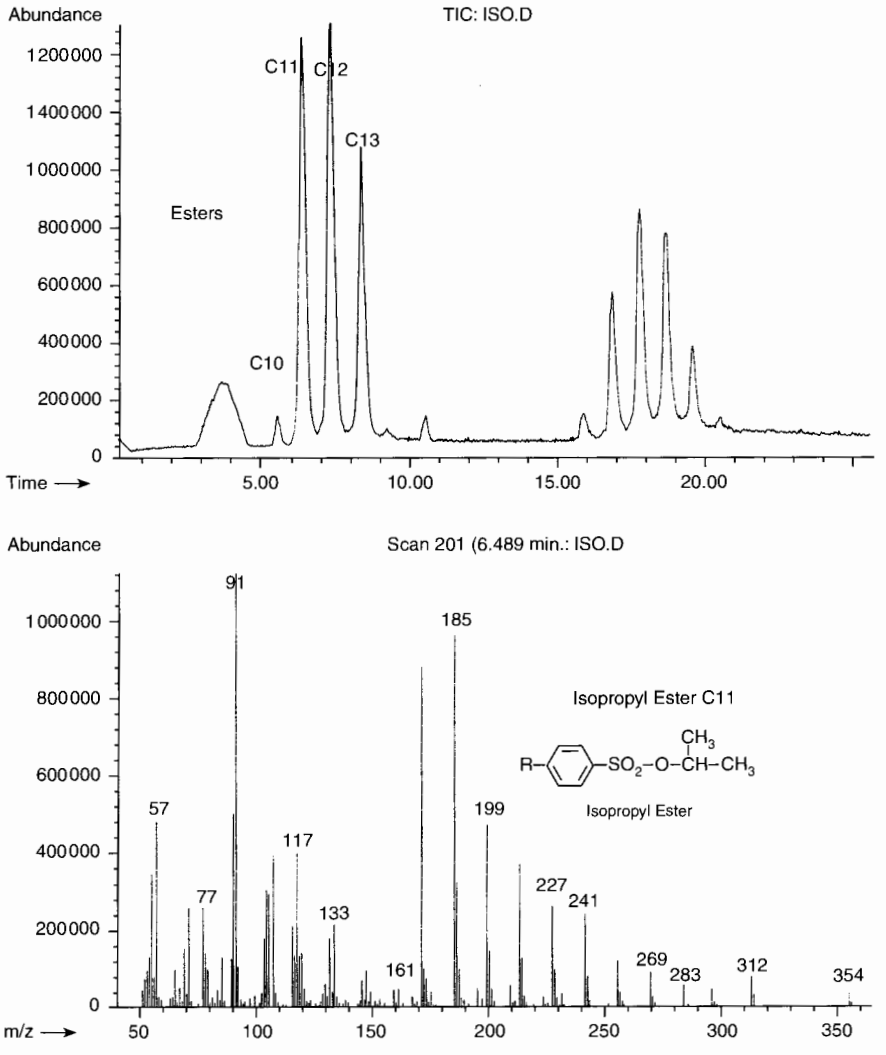


Fig. 5. LC-MS-spectrum of a free oil sample extracted before hydrolysis with isopropanol/water

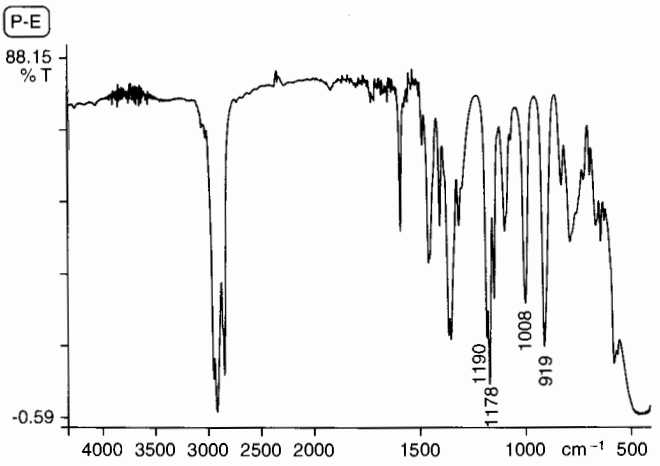


Fig. 6. IR-spectrum of a free oil sample before hydrolysis (digestor outlet)

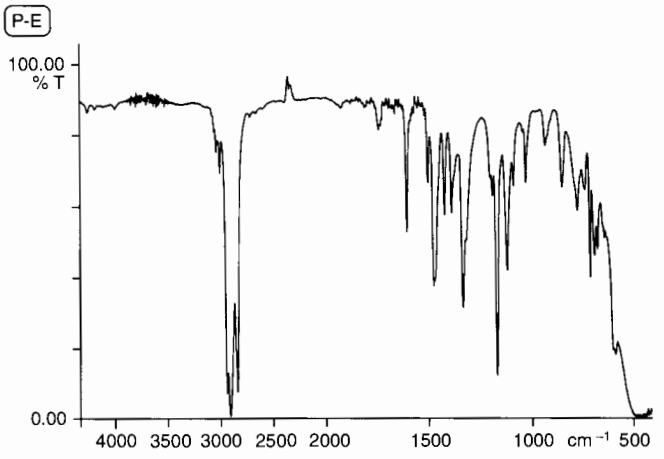


Fig. 7. IR-spectrum of a free oil after hydrolysis (hydrolyzer outlet)

3.2 Identification of sulphones

3.2.1 LC-MS analysis

LC-MS analysis allows to determine the molecular weight of each sulphone. The identification is shown for sulphone 23 on Fig. 8. S23 is the sum of both alkyl tails, in this case of C10 plus C13 or more likely, because of their relative abundance, of C11 plus C12. The seven sulphone peaks can be easily identified (due to the poor MS detection capacity, S20 cannot be detected).

3.2.2 IR spectra

Sulphones were isolated following the method depicted in [3] and analyzed by IR spectroscopy. Figs. 9 and 10 are the spec-

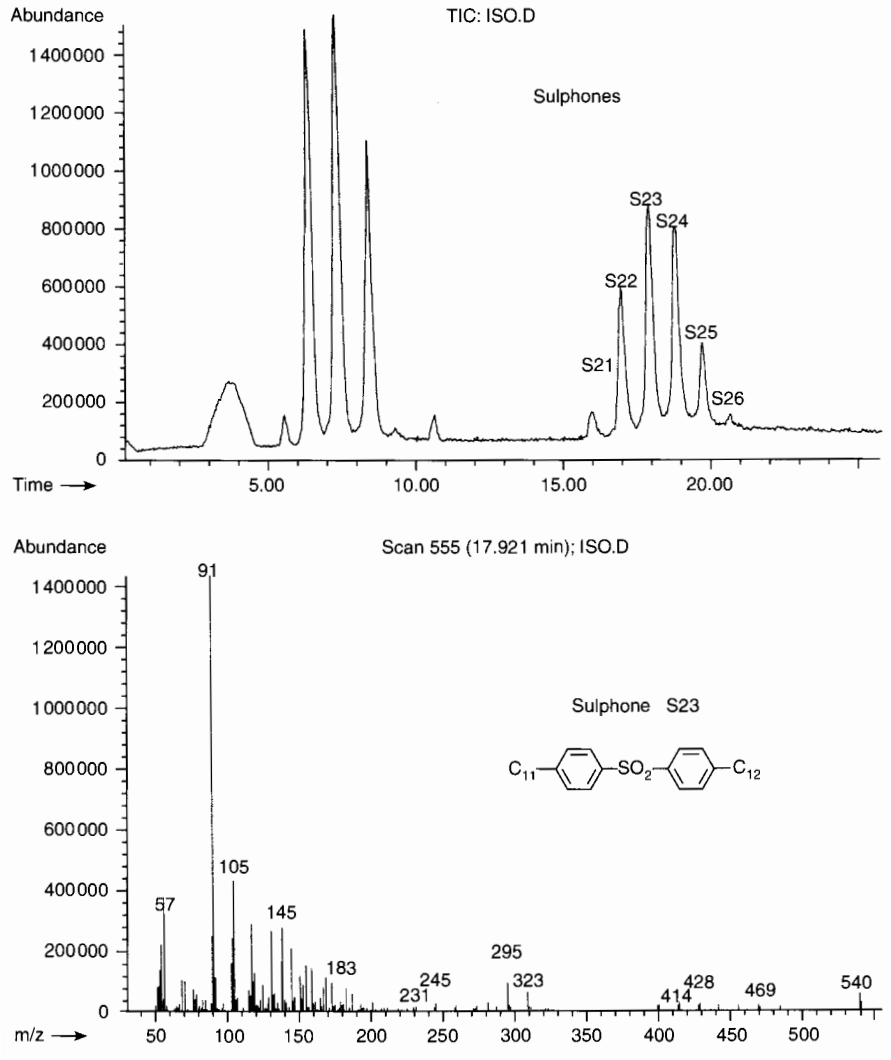


Fig. 8. Identification of sulphone 23 by LC-MS analysis

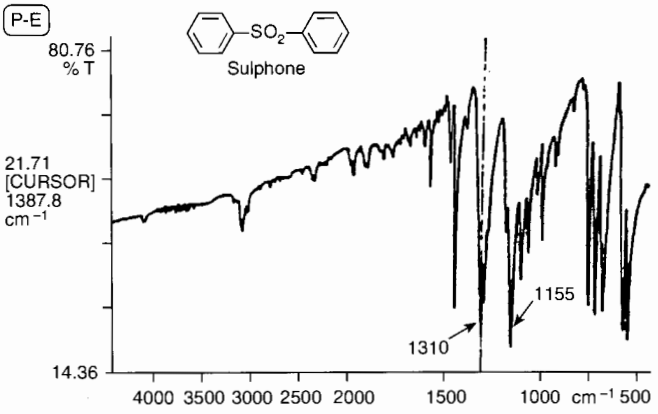


Fig. 9. IR-spectrum of standard diphenyl sulphone

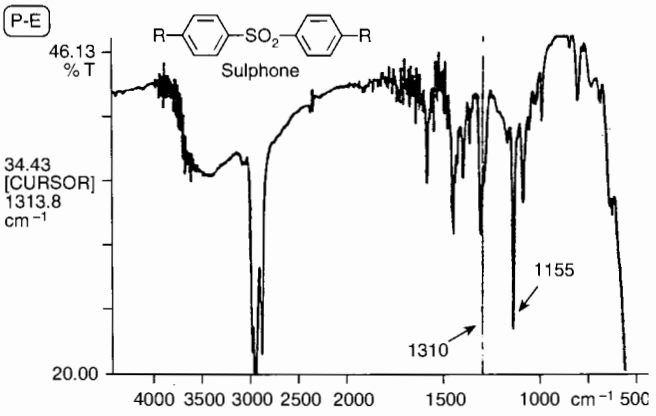


Fig. 10. IR-spectrum of dialkyl-diphenylsulphone

Table 1. Free oil analysis before hydrolysis

	Ethanol 1, Water 2	Ethanol/Water	Water 1, Ethanol 2	% LAB + Sulphones	% total Anhydrides
Sample 1 (labo.)	2 %	1.4 %	0.7 %	0.7 %	2.3 %
Sample 2 (labo.)	2.2 %	1.6 %	0.8 %	0.8 %	2.5 %
Sample 3 (indust.)	3.2 %	2 %	1.4 %	1.4 %	3.2 %
Sample 4 (indust.)	3.2 %	2.3 %	1.5 %	1.5 %	3.1 %

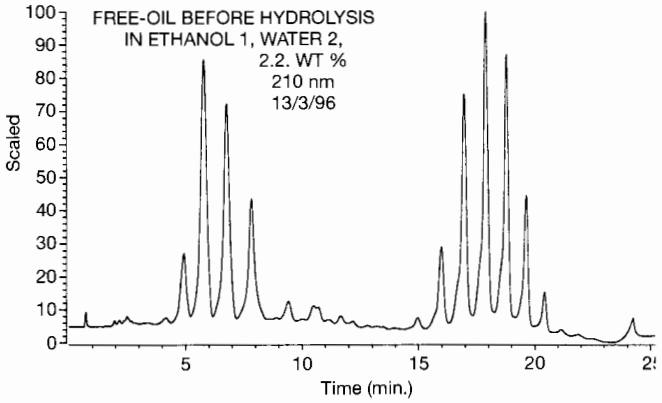


Fig. 11. HPL-Chromatogram of a sample taken before hydrolysis extracted with 1. ethanol, 2. water

tra of standard diphenyl sulphone and of sulphones separated from LAB. The wavelengths corresponding to the characteristic peaks of sulphones are indicated on both spectra.

3.3 Quantitative approach

According to the current free oil extraction method, anhydrides react partially with ethanol (esterification) and partially with water (hydrolysis), hence a new methodology for free oil extraction is needed if a mass balance has to be run.

A suitable new method to achieve this purpose is:

First step: Ethanol 1/Water 2

Dissolve the acid sample, before hydrolysis (at the digestor outlet), in ethanol during half an hour (in order to be sure that all the anhydrides have been esterified), then add the amount of water which is necessary for hexane

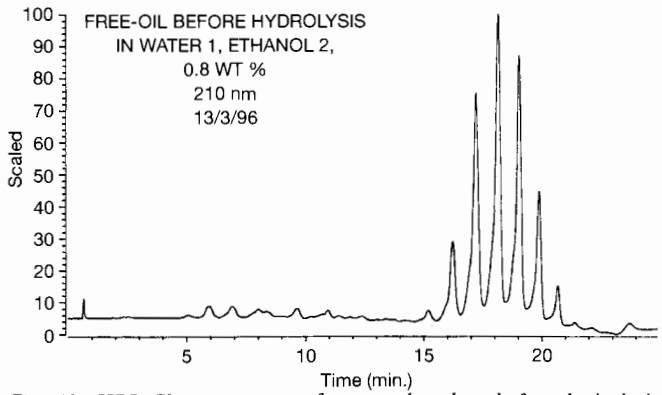


Fig. 12. HPL-Chromatogram of a sample taken before hydrolysis extracted with an ethanol water mixture

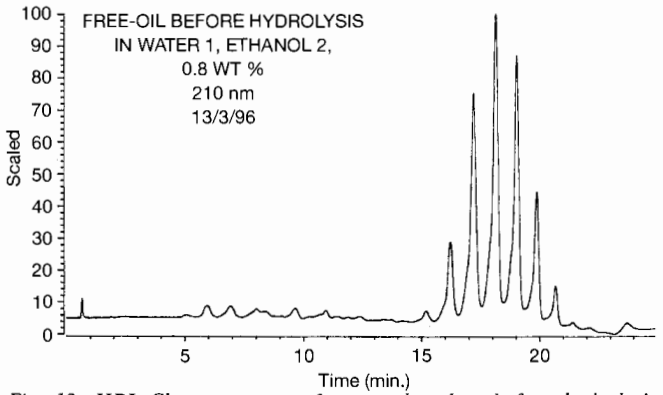
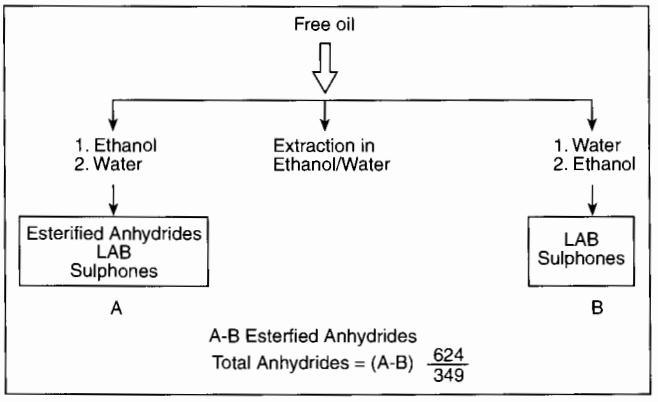


Fig. 13. HPL-Chromatogram of a sample taken before hydrolysis extracted with 1. water, 2. ethanol

extraction. After hexane evaporation, the extract will contain esters, LAB and sulphones. The only reaction taking place should be the esterification (Scheme 3).

Second step: Water 1/Ethanol 2
Dissolve the acid sample, before hydrolysis, in water during half an hour, then add the amount of ethanol to achieve hexane extraction. After hexane evaporation, the extract will contain LAB and sulfones (because all the anhydrides have been hydrolyzed). In this case the single reaction should be hydrolysis (Scheme 3). As an alternative this second step can also be carried out by determining the free-oil content after hydrolysis (hydrolyzer outlet), following the existing extraction procedure.

The difference between both free oil amounts corresponds to anhydrides esterified. Scheme 4 shows a mass balance, assuming an average molecular weight of 624 for anhydrides and 349 for esters.



Scheme 4. Mass balance of free oil

Various samples, from either our industrial sulphonation plant or from different experiments in our laboratory scale sulphonation unit, were analyzed using the methodology herein described. Anhydrides and LAB plus Sulphones were calculated, some of the results are given in Table 1.

Free oil compositions extracted from the same acid sample (sample 2 (labo)) using the three extraction methods are plotted on Figs. 11, 12 and 13. As it can be observed, there is a perfect correlation between quantitative (Table 1) and HPLC qualitative analysis. Free oil and esters are highest with ethanol 1/water 2, then both decrease with ethanol/water mixture and finally reach the minimum value with water 1/ethanol 2 because anhydrides have been fully hydrolyzed.

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