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Linear Alkylbenzene Sulphonates: Biodegradability and Isomeric Composition

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Although on a global level, soap is still used more than surfactants, the wide variety of processes in which surfactants are incorporated has resulted in a spectacular increase in their consumption, which has grown from about $13 \cdot 10^6$ tons in 1977 to $18 \cdot 10^6$ tons in 1995 (Granados 1996). Of this total, some 1.5 million tons correspond to linear alkylbenzene sulphonates (LAS), which means that this is the world's leading type of surfactant in terms of consumption volume.

LAS (Figure 1) are sold in the form of a mixture of homologues in which the length of the alkyl chain varies between 10 and 14 carbon atoms (C10-LAS to C14-LAS). The proportions of these five homologues in the various commercial formulations depend on the specific application of the detergent product.

Each homologue in turn presents a set of isomers as a function of the position occupied in the alkyl chain by the sulphophenyl group; the number and proportion of these isomers is a factor that depends on the conditions of synthesis of the surfactant (Valtorta et al. 1989).

Some authors (Swisher 1963; Wickbold 1964) have found that the isomers of LAS that degrade most easily are those in which the terminal methyl group is positioned furthest from the sulphophenyl group. The explanation for this phenomenon, known as the "distance principle", is based on the steric effect that the aromatic group exerts over the methyl terminal end of the alkyl chain where the process of biodegradation commences (Roberts 1991; Schoberl 1989) (Figure 1).

This effect has been subsequently confirmed by several authors (Roberts 1991; Bayona et al. 1986; Pecenik et al. 1984). Furthermore, LAS monitored in natural waters (Terzic et al. 1992) have been shown to present a predominance of the shorter-chain homologues. Similar effects on the distribution of homologues and isomers of LAS in natural waters are found to be the consequence of processes of physico-chemical division between sediments and the dissolved phase (Amano and Fukushima 1993).

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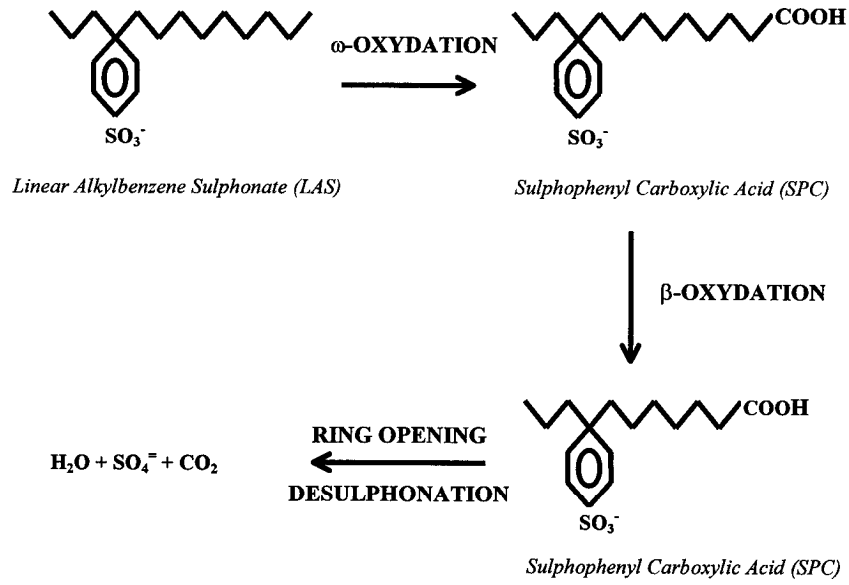

Figure 1. LAS Biodegradation pathway.

This finding, taken together with the fact that some authors have found deviations in the actual biodegradation of LAS from that predicted by the distance principle (Divo and Cardin 1980; Larson 1990), leads one to consider that this principle may be dependent in some way on the conditions of the medium or on the variables of laboratory tests.

The aim of this study is to determine whether any dependency exists between test variables such as temperature or initial concentration of the surfactant, and the selectivity of the LAS biodegradation process towards higher homologues and terminal isomers ; a commercial formulation of this surfactant and a natural mixed microbiota represented by a river water have been used for the purpose of this study.

MATERIALS AND METHODS

The test method employed was the "river die away" test (Weaver and Coughlin 1964), using water taken from the River Guadalete, in the SW of the Iberian Peninsular.

Six different tests were performed, using glass flasks of 6L capacity, into which were poured 4L of previously decanted river water ; this had been collected from the river on the day of commencement of the tests. Subsequently, according to the conditions selected for each test, the correct quantity of surfactant material was added and the flasks were stoppered with hydrophobic cotton. The flasks were then left under the corresponding temperature conditions and in darkness.

The test conditions selected were : Test 1 : 5 mg LAS/L, 21°C ; Test 2 : 10 mg LAS/L, 21°C ; Test 3 : 20 mg LAS/L, 21°C ; Test 4 : 20 mg LAS/L, 7°C ; Test 5 : 20 mg LAS/L, 13°C ;Test 6 : 20 mg LAS/L, 25°C.

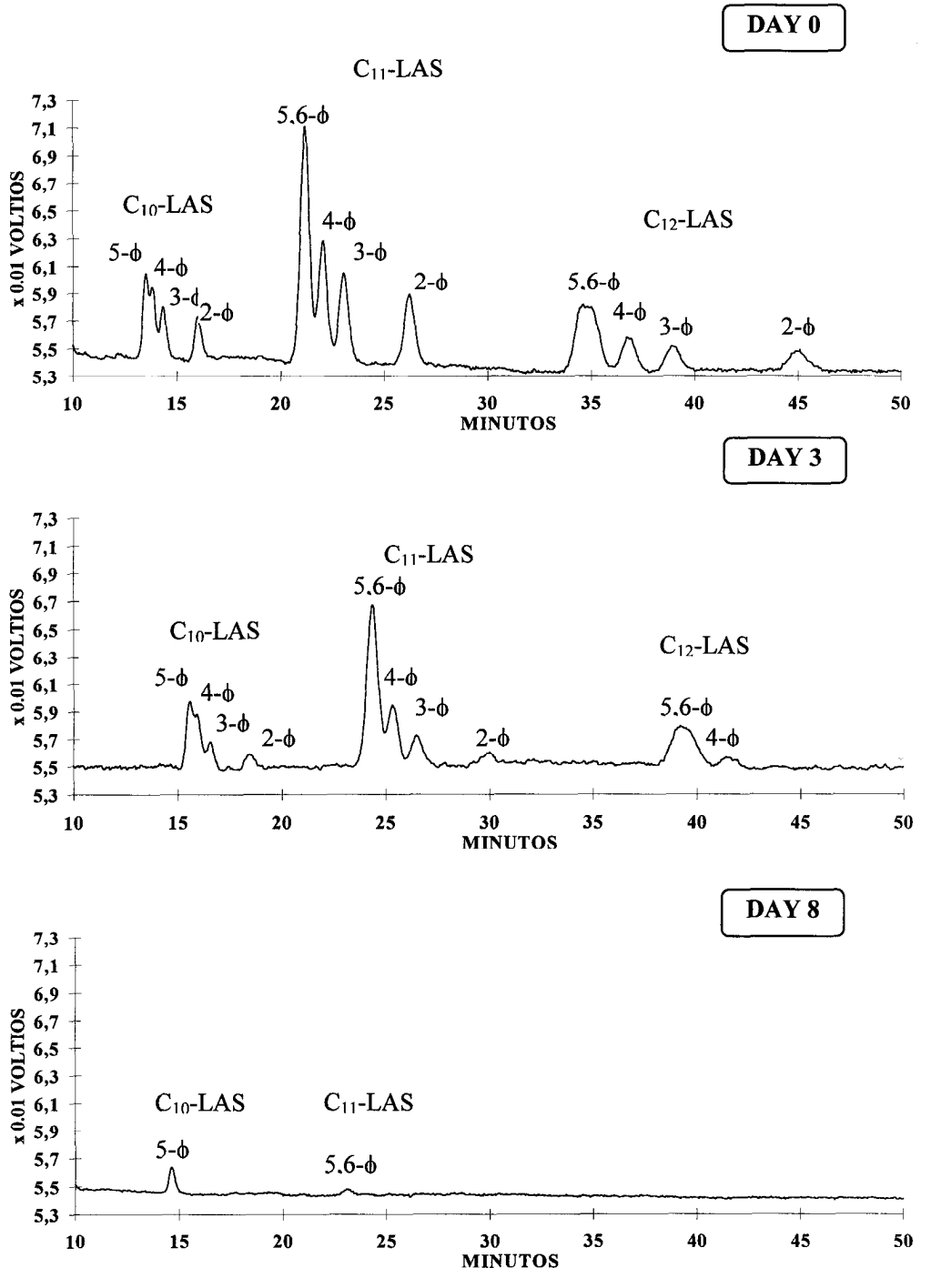

Figure 2. LAS chromatograms corresponding to days 0, 3 and 8 from Test 3

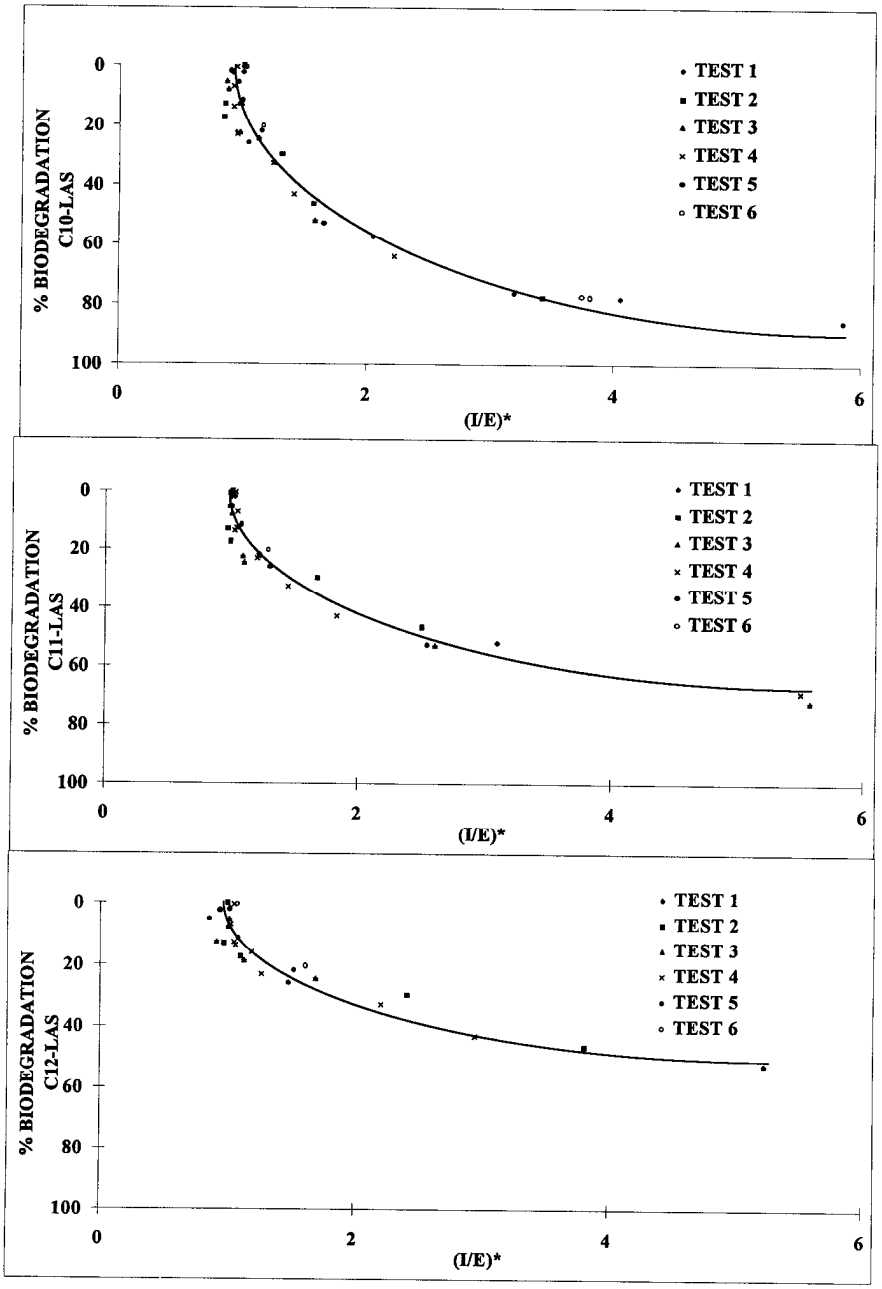

Figure 3. Evolution of the (I/E)* ratio in relation to the percentage of biodegradation reached, by each LAS homologue, under the different test conditions.

The surfactant used was a commercial formulation of LAS provided by PETRESA , Spain, with the following molar distribution of homologues:

C_{10}-LAS :18% ; C_{11}-LAS :51% ; C_{12}-LAS :31%.

After homogenization of the flask content, a sample of 5 mL from each Test was taken periodically ; each sample was filtered through a Waters Nylon filter of 13 cm diameter and 0.2 pm pore size, for subsequent analysis.

The separation and quantification of the different isomers of the commercial formulation of LAS were performed by Reversed Phase High Performance Liquid Chromatography (RP-HPLC). The equipment consisted of a Waters 510 liquid chromatograph fitted with a Waters Model U6K injector and a Waters 470 fluorescence detector.

The chromatographic conditions used were based on the method proposed by Nakae et al. (1981), as follows :

Column : 250 x 45 mm Lichrospher 100 RP18 (5 µm)
Mobile phase : Acetonitrile/water (45 :55) 0.1 M sodium perchlorate
Flow rate : 1 mL/min.
Detector : Fluorescence lem 290 nm. λ_{ex} 232 nm.
Injection volume : 50 µL

The HPLC quality acetonitrile was supplied by Scharlau SA., and the water was prepared from deionized water which was also treated in a Millipore purification unit (Milli-Q water). The sodium perchlorate was supplied by Fluka Chemie AG.

RESULTS AND DISCUSSION

Taking as an example the chromatograms for the various stages of the biodegradation process in Test 3 (20 ppm, 21 °C)(Figure 2), it can be observed that, after three days of test, in all the homologues, the signal corresponding to the 2-sulphophenyl isomer is significantly reduced; this reduction is sharper for the higher homologues. In the case of the C12-LAS homologue, not only has the signal corresponding to the most terminal isomer disappeared but so too has the signal for the 3-sulphophenyl isomer. After eight days of test, the only signals that appear are the two corresponding to the homologues of 10 and 11 carbon atoms, specifically for the isomers in central positions. Analogous observations can be made for the other five tests. This finding seems to indicate that the distance principle applies under the different conditions tested (Swisher 1987).

Three representations of the results obtained are given as Figure 3. These show the evolution of the isomeric ratio (I/E)* compared with the percentage of biodegradation reached for each homologue of LAS under the different test conditions.

$$\frac{I}{E} = \frac{\sum Isómeros\,in.}{\sum Isómeros\,ex.} = \frac{Area(6\phi) + Area(5\phi)}{Area(4\phi) + Area(3\phi) + Area(2\phi)} \qquad \text{(Equation 1)}$$

Area (iϕ) = The area of the chromatographic signal corresponding to the isomer i.

If the ratio I/E is normalized, by dividing it by the value of I/E on day 0 of the test, the resulting expression is :

$$relación\left(\frac{I}{E}\right)^{*} = \frac{\left(\frac{I}{E}\right)}{\left(\frac{I}{E}\right)_0} \qquad \text{(Equation2.)}$$

Where :

(I/E)* = the normalized isomeric ratio

$O/E)_d$ = the isomeric ratio corresponding to day *d* of the test

$(I/E)_0$ = the isomeric ratio corresponding to day 0 of the test

The percentage of biodegradation is calculated by the following expression :

$$\%\, Bdg.LAS = \left(\frac{[LAS]_0 - [LAS]_d}{[LAS]_0}\right) x100 \qquad \text{(Equation 3)}$$

Where :

$[LAS]_0$ = initial concentration of LAS

$[LAS]_d$ = concentration of LAS on day d of the test.

As can be seen in Figure 3, the evolution followed in the different tests performed is similar.The value of the ratio (I/E)* becomes greater in proportion as the the percentage of biodegradation reached by the various homologues increases ; in other words, there is an increase in the proportion of internal isomers with respect to the initial isomeric ratio of the product.

With the (I/E)* curves, the objective is to estimate the degree of biodegradation of LAS in environmental samples, under the assumption that the results of the laboratory experiments are valid for natural media. This assumption appears reasonable, given that the medium used in the experiments is river water, which contains the same nutrients, microbiota and organic material that may typically be found in this compartment of the natural environment. Consequently, it is considered that the biological process that takes place in the reactors is similar those occurring in the natural medium.

Of course, the water temperature, the redox potential, the LAS concentrations, etc., may affect the metabolic capacity of the microbiota (Swisher 1987). Therefore, the rate and range of the degradation of LAS in the natural medium may differ from that observed in the laboratory, but the differences in the microbial activity that could be produced as a result of the alteration of variables such as the temperature or the initial concentration of LAS do not affect the selective biodegradation of isomers and homologues, as may be observed in Figure 3. Such results are found to be similar to those obtained previously by other authors (Takada et al. 1990) for linear alkylbenzene (LAB) in waste waters.In addition, it can be observed in Figure 3 that, for the same percentage of biodegradation, the isomeric ratio is greater for higher homologues. This indicates that, for homologues with shorter chain length, the difference in biodegradability between internal and external isomers is less than for higher homologues.

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