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Primary Biodegradation Kinetics of Anionic Surfactants in Marine Environment

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The process of surfactant biodegradation has received little attention in marine environments. One of the reasons for this has been the belief in the sea's great powers of dilution and self depuration another, is that most papers on this subject have been on inland waters, where the effects of effluents containing detergents are more spectacular. Nevertheless, the outflow from rivers and sewage outlets on the coasts themselves have driven surfactant matter concentration to very high levels in some densely-populated coastal ecosystem. The presence of these subtances in the medium has a remarkable effect on marine fauna, especially in its first stages of development (Hidu 1965; Walne 1968; Granmo 1972), so that the biological productivity of many such ecosystem may be endangered.

Most of the studies made in fresh water conclude that biodegradation follows a first-order kinetic. However, in sea water, the differences in number and type of micro-organisms can imply a modification of the biodegradation process.

Here we study, from a kinetic standpoint, primary biodegradation of 5 anionic surfactants in a marine environment. The surfactants are a representative selection of the various types used in the manufacture of detergents and other commercial cleaning agents. The experiments were conducted in the presence of sediments, since it has been established that this subtantially increases the process of surfactant degradation (Sales et al. 1984).

MATERIALS AND METHODS

The experiments were conducted in duplicate, using a modification of the River Water Test (Swisher 1970), described elsewhere (Sales et al. 1984). Series of 250 ml flasks were used, containing 100 ml sea-water (S=36.2 $^{o}/_{oo}$) and 25 g of wet sediment (40 % solids). One mg of surfactant was added to each flask to obtain concentrations similar to those found near urban sewage outlets in the Bay of Cadiz (Flores et al. 1980). Analysis of surfactant matter was carried out in

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Table 1. Characteristics of surfactants studied.

Surfactant	Denomi-nation	Characteristics	Surfactant matter (%)	Main use
Alkyl-bencene-sulfonate	LAS	C_{12},linear chain	90.3	domestic detergents
Alkyl-sulfate	DS	C_{12},linear chain	>99	analytical standard
Alkyl-eter-sulfate	AES	C_{13},branched chain	30	cosmetic,shampoos
Diisooctil-sulfosuccinate	DOS	C_{16},moderately branched	>99	analytical standard
Isohexil-isopentil-sulfosuccinate	HPS	C_{11},highly branched	99.7	in disuse

duplicate according to Abbot's method (Abbot 1962). To measure concentration in the sediments, surfactants were extracted with a mixture of CH_3OH and 2N NH_4OH at a volume ratio of 2 to 1 (Sales et al. 1984).

Table 1 shows the surfactants selected for study, along with their degree of purity and their common use. The degree of ethoxylation of the alkyl ether sulphate used was 3 moles of ethylene oxyde per mole of alcohol. For LAS, biodegradation was studied at 5, 10, 15, 20 and 25°C. The other surfactants were tested at 25°C. The sea-water and sediments used were taken from a sound near the Bay of Cadiz where pollution levels are low (Sales et al. 1983; Establier et al. 1985).

All the material used for sampling and testing was sterilized beforehand and the sea-water was saturated with oxygen before the start of the experiments.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the relative quantity of undegradated surfactant, defined as the ratio between the actual and the initial surfactant quantity (C/C_0), vs time. The surfactants studied show subtantial differences in behaviour. There are also appreciable differences in the way in which LAS is degradated, depending on the temperature at which the test were conducted.

To determine kinetic equation for the biodegradation process, several polynomial expressions -from zero to 6th degree- were tested for the degradation rate as a function of the residual quantity of surfactant. Data were processed on a DIGITAL PDP-11 computer. Degradation rate was calculated from the ratio $(C_i-C_{i-1})/(t_i-t_{i-1})$. This value obtained is taken as that at which degradation occurs when the quantity of residual surfactant is C_i, which is given by $(C_i + C_{i-1})/2$. In these expressions C_i and C_{i-1} are the surfactant quantities present at times t_i and t_{i-1}, respectively.

For HPS and LAS at temperatures of 25°C and $\leq$15°C respectively, zero degree polynomial functions with $0.95<r<0.97$ were fitted

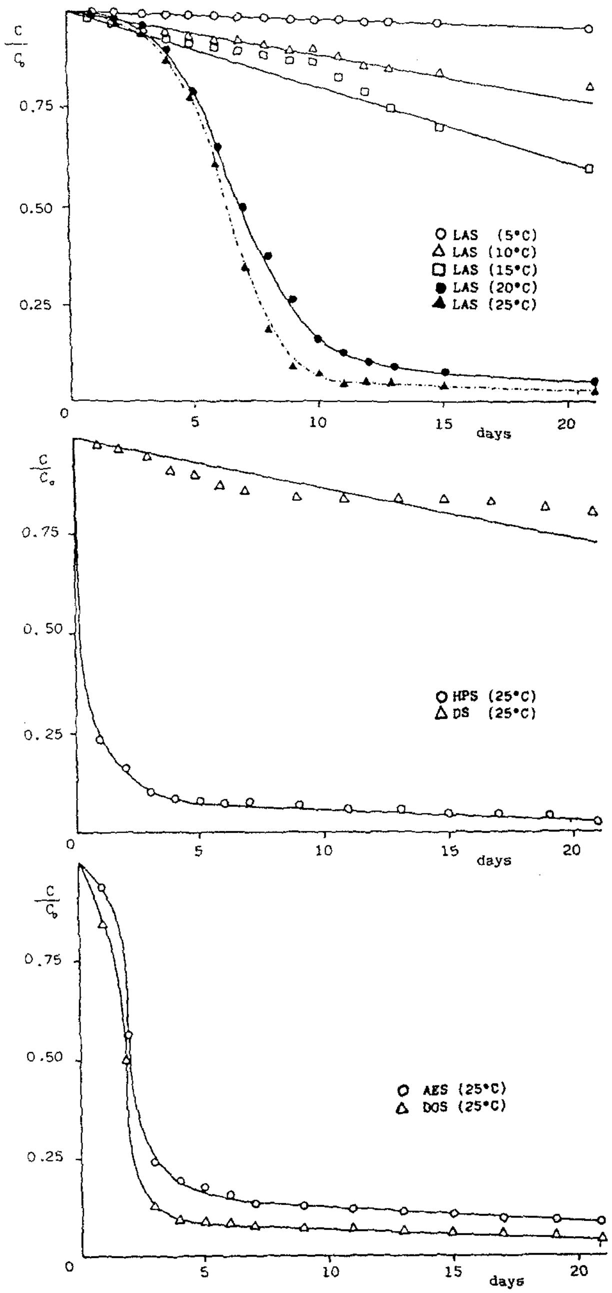

Figure 1. Residual relative quantity of surfactant (C/C_0) versus time (C and C_0 are, respectively, actual and initial quantity of surfactant). Analysis where carried out by triplicate.

to be the best. A first degree polynomial is the most adequate for DS. Moreover, the independent term was found to be statistically not different from zero; therefore, primary biodegradation of DS followed a first-order kinetic. The best results for LAS (20 and 25°C), DOS (25°) and AES (25°C) were obtained by a 2nd-degree polynomial such as

$$\gamma = -\frac{dC}{dt} = ac \quad +bC + d \qquad |1|$$

where a, b and d are adjustment coefficients obtained from the least square method.

The validity of equation |1| was tested by comparison of the values of experimentally found surfactant quantity at time t with the theoretical values calculated by integration of |1|. This integration gives

$$C = \frac{C_0 m - mn + (mn - C_0 n)\exp(pt)}{C_0 - n + (m - C_0)\exp(pt)} \qquad |2|$$

where $p=(b^2-4ad)^{1/2}$, $m=-(p+b)/2a$, $n=(p-b)/2a$ and C_0 are the initial quantity of surfactant.

The results obtained are shown in fig. 2. It can be seen that the points corresponding to each set of experiments show a linear regression whose slopes are close to 1 and the intercepts do not deviate significantly from 0.

The values of the coefficients a, b and d of the kinetic equation are summarized in table 2. These coefficient values were calculated from the parameters p, m and n of eq. |2| for those cases in which the kinetic equation is given by |1|. In other cases (rate expression of zero- or first-order), the coefficients were calculated using the adequate integrate kinetic equation.

Cases in which the equation of degradation rate can be expressed by an equation of the type given in |1|, can also be written as

$$\gamma = -\frac{dC}{dt} = kC(1-\beta C) + K \qquad |3|$$

where $k=b$, $\beta=-a/b$ and $K=d$.

Equation |3| may be related to the evolution of the number of micro-organisms, if we accept that Gaden's hypothesis (Gaden 1959), formulated for a fermentation process, can be extrapolated to biodegradation of surfactants. This hypothesis establishes that the increase in cellular biomass:

$$-\frac{d(\text{substtrate})}{dt} = K''' \frac{d(\text{cellular biomass})}{dt}$$

If we admit a direct relation between the variation in the mass of cells producing degradation and the increase in the number of micro-organism colonies (n), results:

Table 2. Values of coefficients of equation |1| for the different surfactants studied

Surfactant	T(°C)	a	b	d
LAS	5	---	---	4.15
LAS	10	---	---	21.50
LAS	15	---	---	40.20
LAS	20	$-2.60\ 10^{-4}$	0.59	-56.01
LAS	25	$-2.90\ 10^{-4}$	0.64	-23.34
DS	25	---	0.11	0.29
AES	25	$-1.48\ 10^{-3}$	1.91	-107.81
DOS	25	$-1.25\ 10^{-3}$	1.65	-176.49
HPS	25	---	---	8.29

$$-\frac{dC}{dt} = K''\frac{dn}{dt} \qquad |4|$$

integrating

$$C = -K''n + K' \qquad |5|$$

where $K' = K''n_0C_0$ $[C_0 = C(0)$ and $n_0 = n(0)]$.

Hence from |4| and |5| we find that eq. |3| is also given by

$$\frac{dn}{dt} = k'n(1-\delta n) + K_0 \qquad |6|$$

where $k' = -(2aK'+b)$, $\delta = aK''/(2aK'+b)$, $K_0 = (aK'^2 + bK' + b)/K''$ and a, b and d are coefficients of equation |1|.

Equation |6| bears a close resemblance to Volterra's modification (Bailey and Ollis 1980) of the model proposed by Pearl and Reed (1920) (where $K_0=0$) for bacterial growth in a biological reactor operating discontinuously. In this last model, δ^{-1} would represent the stationary bacterial population (n_s) to be reached when the substrate was exhausted. In our case, K_0 may be assimilated to a mean value of the complex term added by Volterra to the previous model.

When $K_0 < 0$, Volterra's model predicts that the number of micro-organisms decrease after attaining a maximum value of n_s. Figure 3 shows the results of the aerobic micro-organisms recount. These are chiefly responsible for biodegradation in the conditions prevailing in the tests. It can be seen that Volterra's prediction is valid for those tests that follow the kinetic equation given in |1| or |3|.

For small absolute values of K and K_0, equations |2| and |6| correspond to two inverted sigmoidal curves. By analogy, β^{-1} in

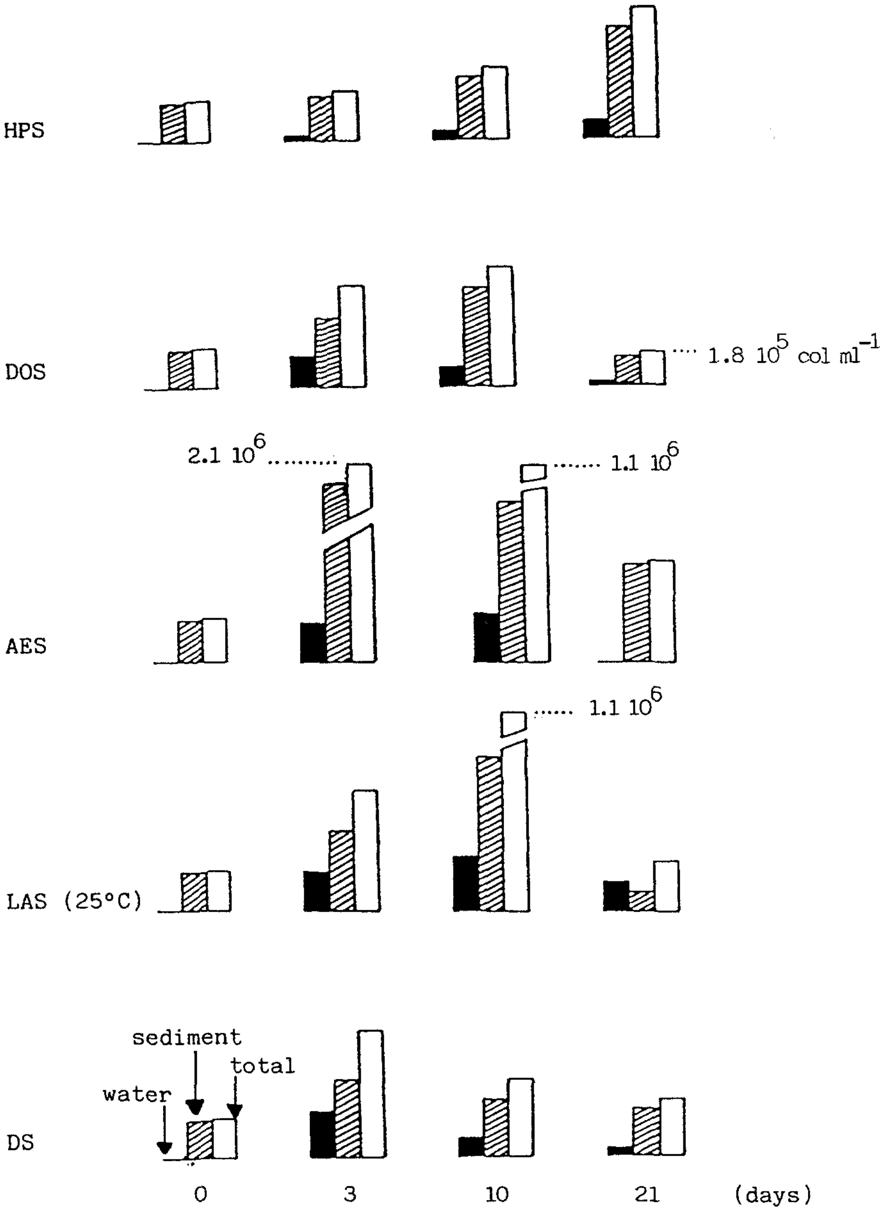

Figure 3. Evolution of number of aerobic micro-organism colonies during degradation of the surfactants studied. All the grapho are in the same scale.

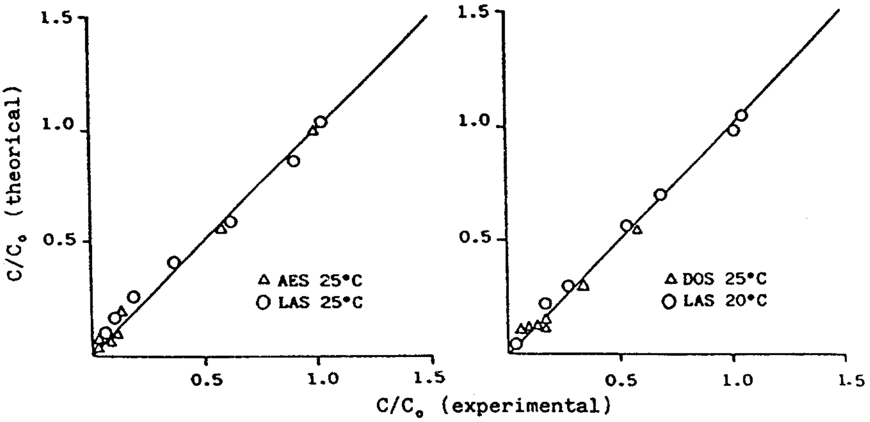

Figure 2. Chart of theoretical quantity of surfactant derived from equation |2|, vs experimental values.

equation |2| ought to represent the initial quantity of surfactant used in each test. In general, the values of β^{-1} obtained differed from C by less than 5%.

The degradation of LAS at temperatures below 15°C, and HPS at 25°C, occurs with a zero order kinetic. In the first case, this can be attributed to the fact that bacterial activity decreases significantly when temperature descends, so that the rate of surface-activity loss becomes independent of the amount of surfactant in the medium. In the other case, this fact may be connected with the scant biodegradability of the surfactant as a consequence of its highly branched aliphatic chain (Ryckman 1975).

The surfactant concentration decreases exponentially from the first day of test for DS (first order kinetic). This coincides with the findings of other authors in river water (Ruschemberg 1963) and it can be attributed to the ease with which its surface-activity decreases as a consequence of the hydrolysis of the sulphate group. This hydrolysis is caused by the action of specific enzymes that exist in the medium. This fact produces the plot of residual quantity of surfactant vs time (se fig. 1) which does not show the effects of a lag period of the bacterial flora.

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