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ON-LINE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY ANALYSIS OF NON-IONIC SURFACTANTS

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SUMMARY

Non-ionic surfactants of the alkylphenolethoxylate and oxoalcoholethoxylate classes were analysed by on-line liquid chromatography–mass spectrometry using a mechanical transport interface. Information on the distribution of homologues and the presence of impurities was obtained. The method can be used to study the primary biodegradation of non-ionic surfactants.

INTRODUCTION

Non-ionic surfactants comprise the second most important class of surfactants after the anionic surfactants. The main types are alkylphenolethoxylates, *e.g.* $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$, and oxoalcoholethoxylates, *e.g.* $C_mH_{2m+1}O(CH_2CH_2O)_nH$, which are produced by condensation reactions between ethylene oxide and the appropriate alkylphenol or fatty alcohol. They are usually manufactured as a mixture of homologous compounds which differ in the length of the ethoxylate or the alkyl chain. A variety of methods has been employed for their analysis[1,2], among which liquid chromatography (LC) plays an important role because it gives direct information on the distribution of chain lengths. Alkylphenolethoxylates can be readily identified by UV detection but oxoalcoholethoxylates are UV-transparent. Thus esterification with 3,5-dinitrobenzoyl chloride has been proposed for the analysis of the latter[3].

This study reports the direct identification of oxoalcoholethoxylates by on-line LC–mass spectrometry (LC–MS). Moreover, this technique permits straightforward peak assignment even in those cases were UV detection is not possible.

EXPERIMENTAL

A non-commercial quadrupole mass spectrometer was used for all measurements. The mass spectrometer was equipped with the new Finnigan moving-belt LC–MS interface. With this interface the moving belt extend into the ionization

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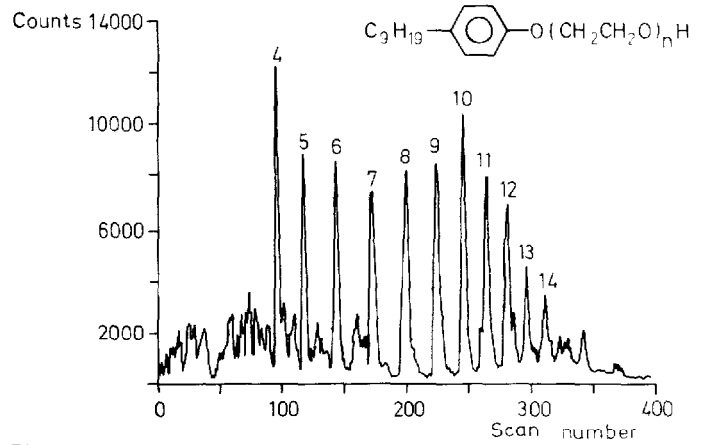

Fig. 1. Total ion current trace of a nonylphenolethoxylate measured under CI conditions. The number of ethylene oxide units is indicated on each peak.

chamber of the mass spectrometer. The solvent heater was kept at 120°C and the sample heater at 250°C. The ion source temperature was 230°C. Mass spectra were obtained in the electron impact (EI) or chemical ionization (CI) mode with isobutane as the reagent gas.

LC separation was carried out according to Van der Maeden *et al.*[4], with a Varian liquid chromatograph (type 5020) and a 250 × 4.6 mm aminopropyl column (Servachrom) with 5-μm particle size at a solvent flow-rate of 1 ml/min. A solvent gradient from 2% to 50% of solvent B in A in 60 min was used (solvent A was 20% tetrahydrofuran in *n*-hexane, solvent B was 10% water in 2-propanol).

Octylphenolethoxylate (Triton X100) was purchased from Merck, nonylphenolethoxylate (Akopal N060) from Hoechst and cetylethoxylate (Brij 56) from Serva. All samples were used as supplied.

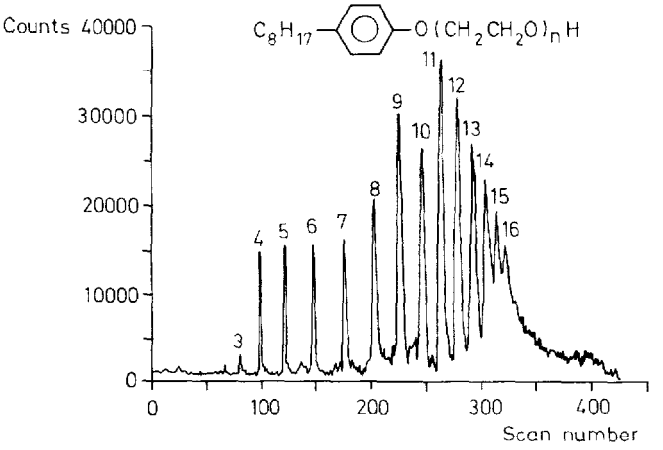

Fig. 2. Total ion current trace of an octylphenolethoxylate measured under CI conditions.

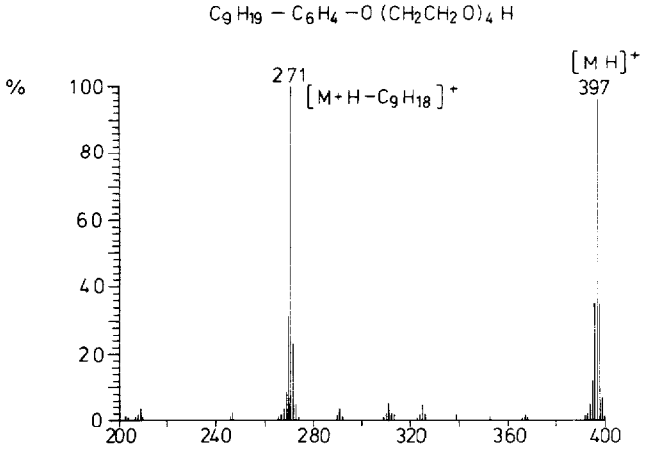

Fig. 3. CI (isobutane) mass spectrum of C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_4H$.

RESULTS AND DISCUSSION

Fig. 1 shows the total ion current trace of a nonylphenolethoxylate mixture measured under CI conditions with isobutane as reagent gas, and Fig. 2 the corresponding trace for an octylphenolethoxylate mixture. The various homologous are well separated. The peak assignment is based on the individual mass spectra.

The CI mass spectra are dominated by protonated molecules. In addition, an abundant fragment formed by loss of nonene (octene in the case of octylphenolethoxylate) is observed with all lower homologues with up to six ethylene oxide units. This is shown in Fig. 3 for the homologue with four ethylene oxide units. This fragment is unimportant with higher homologues. Instead a fragment at *m/z* 291 (*m/z* 277 in the case of octylphenolethoxylate) is observed, which is formed by cleavage of the C–O bond in the second ethylene oxide unit (Fig. 4).

Fig. 5 represents the EI spectrum of one of the homologues of nonylphenolethoxylate. The molecular ion is clearly discernible. The upper mass range is dominated by a fragment at *m/z* 311 formed by loss of a hexyl radical. This suggests that the alkyl chain is predominantly branched, as shown in Fig. 5.

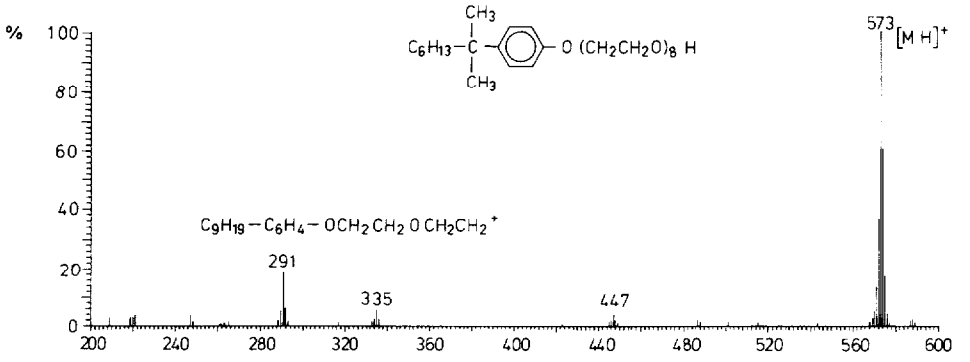

Fig. 4. CI (isobutane) mass spectrum of C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_8H$.

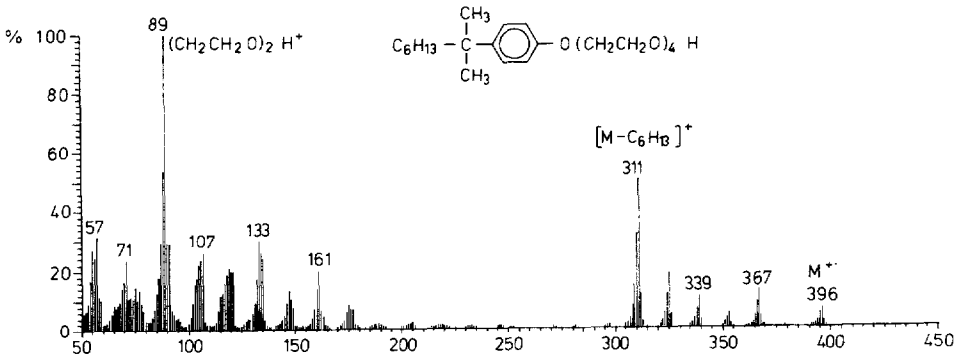

Fig. 5. EI mass spectrum of C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_4H$.

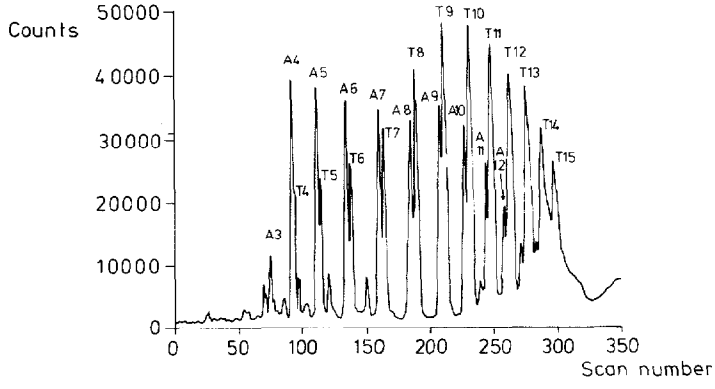

Fig. 6. Total ion current trace of a mixture of octylphenol- (T) and nonylphenolethoxylate (A) measured under CI conditions.

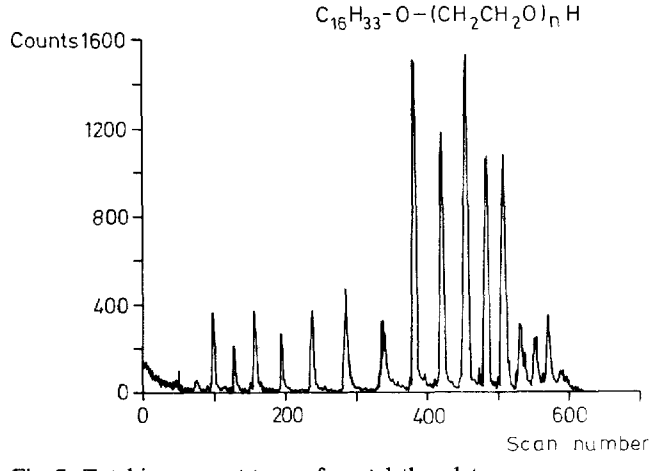

Fig. 7. Total ion current trace of a cetylethoxylate.

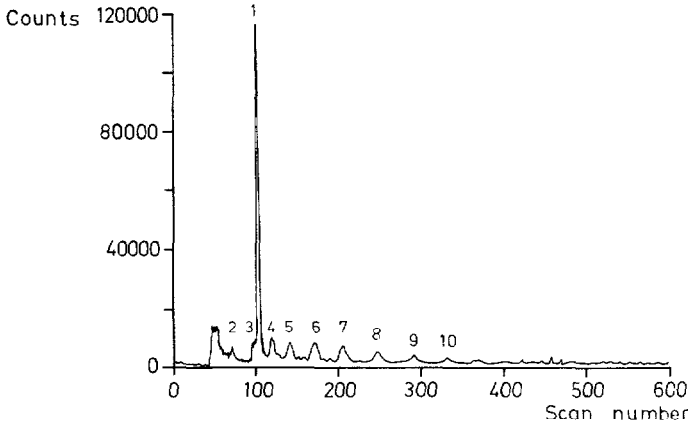

Fig. 8. Total ion current trace of a nonylphenolethoxylate after 3 days of biodegradation in surface water measured under EI conditions. Peak 1 correspons to C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_2H$, and peaks 2–10 to $(C_9H_{19})_2$–C_6H_3–$O(CH_2CH_2O)_nH$.

Fig. 6 shows the total ion current trace of a mixture of an octylphenolethoxylate and a nonylphenolethoxylate. Only a partial separation of the two components is observed with all higher homologues ($n > 5$). Comparison with the UV trace reveals that the distribution of homologues is reproduced at least semiquantitatively.

Fig. 7 shows the total ion current trace of a cetylethoxylate. In this instance the MS detection of the individual homologues is particularly valuable as this sample shows no UV absorption. The corresponding mass spectra are very simple. The CI mass spectra show exclusively the protonated molecule whereas the molecular ion is absent in the EI mass spectra. The EI mass spectra are dominated by unspecific ions of the general formula $(CH_2CH_2O)_nH^+$ in the lower mass range.

Finally we have investigated whether the biodegradation of non-ionic surfactants in surface water can be monitored by this approach. To this end 0.3 g of nonylphenolethoxylate was added to 4 l of river water and the solution stirred continuously. A 50-ml sample was taken after 3 days, evaporated to dryness, dissolved repeatedly in chloroform or tetrachloromethane and analysed by LC–MS. The re-

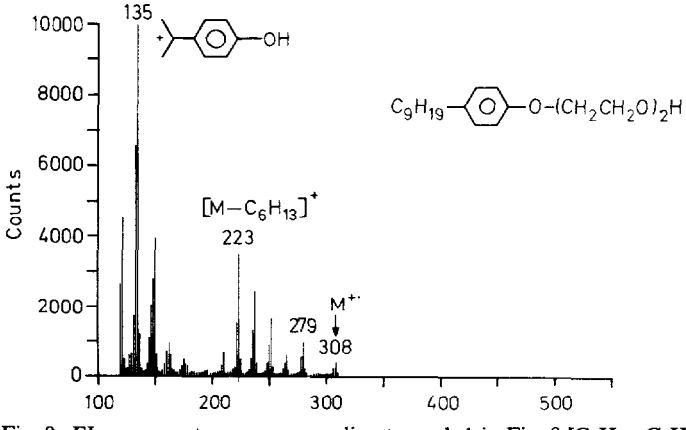

Fig. 9. EI mass spectrum corresponding to peak 1 in Fig. 8 [C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_2H$].

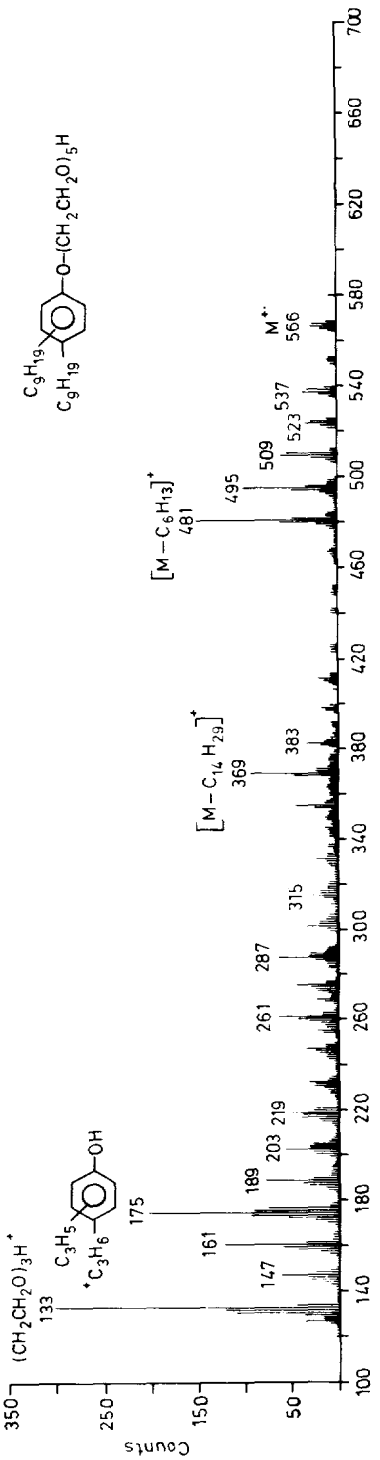

Fig. 10. EI mass spectrum corresponding to peak 5 in Fig. 8 [$(C_9H_{19})_2$–C_6H_3–$O(CH_2CH_2O)_5H$].

sulting total ion current chromatogram shown in Fig. 8 displays mainly one peak. The corresponding EI mass spectrum is shown in Fig. 9. The spectrum allows this peak to be assigned to the homologue with two ethylene oxide units. In addition, Fig. 8 shows a series of peaks of low intensity. The EI mass spectrum corresponding to peak 5 is shown in Fig. 10. It allows this peak to be assigned as dinonylphenolethoxylate. The remaining peaks in this chromatogram are all attributable to dinonylphenolethoxylates. Thus dinonylphenolethoxylate is present in the sample as an impurity. These results demonstrate that the nonylphenolethoxylates are biodegraded to the homologue with two ethylene oxide units within 3 days while no significant biodegradation of dinonylphenolethoxylate is observed within the same period.

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