

Analysis of the Polyethylene Glycol Glucosides and FA Esters Thereof by Atmospheric-Pressure Ionization MS

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ABSTRACT: Polyethylene glycol (PEG) glucosides (PEGG) and the PEGG esters of lauric acid were analyzed by atmospheric-pressure ionization MS (API-MS) with electrospray ionization. Straightforward mass characterization of the complex mixtures could be achieved without prior chromatographic separation. The constituents were identified on the basis of quasi-molecular ions. Individual components could be observed as protonated molecular ions $[M + H]^+$ and/or as their NH_4^+ , Na^+ , or K^+ adducts in positive ion mode. The mass spectrometric investigation showed that mixtures of PEGG consisted of monoglucoside, diglucoside, polyglucoside, and free PEG. The esterification product is a mixture of two types of nonionic surfactants: PEG-laurates and PEGG-laurates. The reasons for distortion of the quasi-molecular ion intensities and the stabilization of adduct ions were discussed. The rapid and highly sensitive API-MS analysis technique proposed here is well suited for direct characterization of complex mixtures and suitable for development as a routine analytical method.

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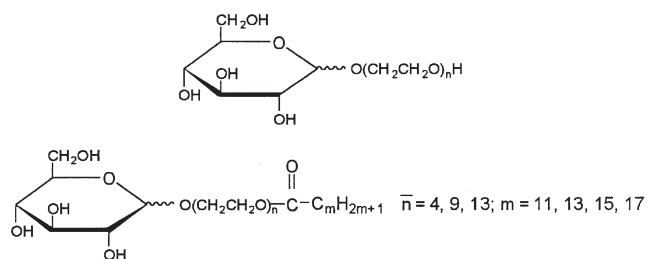
KEY WORDS: Atmospheric-pressure ionization mass spectrometry (API-MS), direct characterization, electrospray ionization (ESI), esterification, fatty acid esters, glucosides, nonionic surfactants, polyethylene glycol (PEG).

Fatty esters of polyalkoxylated polyol glucosides are nonionic surfactants that can be prepared from starch, polyol, ethylene oxide, and FA as starting materials by means of transglycosylation, polyoxyethylation, and esterification (1,2). However, the FA esters of polyethylene glycol glucosides (PEGG) as a nonionic surfactant have not been described in the literature. This new class of nonionic surfactant has been synthesized in our laboratory.

Scheme 1 illustrates a simplified molecular structure of PEGG (3,4) and FA esters thereof. The hydrophilic part of the molecule consists of glucose and ethoxy units. The chain length of the FA varies between C_{12} and C_{18} . In fact, PEGG are complex mixtures containing a large number of species differing in their number of glucose and ethoxy units. Moreover, they can contain diesters, polyesters, and other by-products. It is therefore essential to develop rapid and reliable analytical methods for the detection and determination of these multicomponent surfactant mixtures.

Because of the lack of any chromophoric group in these molecules and their low volatility, HPLC and GC are not well

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SCHEME 1

suited for the analysis of PEGG and esters thereof, particularly if a large variety of reference materials of high purity to identify various components is required.

In recent years, as a result of the development of mass-spectrometric soft ionization techniques, the direct characterization of nonvolatile surfactant mixtures could be achieved without prior chromatographic separation. The FABMS method has been successfully applied to the identification of different classes of surfactants in raw materials (5). Nevertheless, the choice of matrix compound, such as glycerol, is necessary to FABMS and determines whether sample ions can be observed at all, because the unrelated compounds concomitantly present in a complex mixture frequently disturb the ionization of the given sample. The development of matrix-assisted laser desorption ionization/time of flight MS (MALDI-TOF-MS) has allowed the ionization and detection of large biomolecules. Moreover, MALDI-TOF-MS also can be used for the rapid mass analysis of low-M.W. surfactants (6). Similarly, the disturbance presented by concomitantly present unrelated compounds also appears in MALDI-TOF-MS. Atmospheric-pressure ionization MS (API-MS) with electrospray ionization (ESI) overcomes the aforementioned limitations of FAB-MS and MALDI-TOF-MS and is a more rapid and versatile mass-spectrometric approach that is highly suited for the analysis of nonvolatile, highly polar nonionic and anionic surfactants (7–10).

The purpose of our investigation was to develop a simpler and more rapid analytical approach than chromatographic methods to be applied to qualitative analysis of PEGG and esters thereof. Therefore, we chose API-MS with ESI, which is very effective for the analysis of complex mixtures.

EXPERIMENTAL PROCEDURES

Materials. Analytical grade glucose was purchased from Shenyang Chemical Reagents Factory (Shenyang, China); technical blends of PEG200, PEG400, PEG600 oligomers

(where PEG = polyethylene glycol) having, respectively, an average of 4, 9, and 13 ethoxy units were kindly supplied by Liaoyang Aoke Chemicals Company (Liaoyang, China). Analytical grade lauric acid was from Beijing Xudong Chemical Reagents Factory (Beijing, China). PEG200-, PEG400-, and PEG600-glucosides (PEGG200, PEGG400, PEGG600) and laurates thereof were synthesized in the laboratory.

MS. A Hewlett-Packard HP1100 LC-MS system was used in ionization mode, that is, ESI. Data were acquired in full-scan mode in a range of 50–1500 m/z units. In positive ion mode, the ion source conditions were as follows: ion-spray voltage: +3.5 kV; collision-induced degradation voltage: +50 V. For sample preparation, PEGG and the laurates thereof were diluted, respectively, with water and methanol and adjusted with ammonia to pH 8. Sample was infused directly into the ion source at a flow rate of 0.2 mL/min. Nitrogen was used as a drying gas at a flow rate of 5.0 L/min. The drying gas temperature was 350°C, and nebulizer pressure was 137.86 kPa.

RESULTS AND DISCUSSION

Scheme 2 summarizes the pathways for the synthesis of PEGG and laurates thereof and shows the structures of the possible by-products. The first step involves the reaction of glucose with PEG to form PEGG having, respectively, an average of 4, 9, and 13 ethoxy units in a molar ratio of 1:1 in the presence of an acid catalyst. The end of the reaction is found by determining the residual content of reducing sugar with Fehling's reagent. After neutralization, PEGG-laurate were obtained by reacting PEGG with lauric acid in the presence of an alkaline catalyst at elevated temperature (second step).

As shown in Scheme 2, the mixtures of PEGG and esters thereof contain starting materials, such as free PEG from the first step; by-products were PEG-diglucoside, PEG-mono-/di-laurate (a,a'), PEG-monoglucoside-di-laurate (b), PEG-diglucoside-mono-/di-laurate (c,c') as well as the main products, PEG-monoglucoside and PEG-monoglucoside-monolaurate. In addition, in the first step the polyglucosides can be formed through polymerization reactions (not shown in the Scheme 2).

API-MS of PEGG. In electrospray mass spectra, quasi-molecular ions dominate the mass spectra owing to the mild ionization conditions. The compounds are detected as protonated

molecular ions $[M + H]^+$ and/or cluster ions formed by ion–molecule reactions in positive ion mode. This is evidenced by the mass-spectrometric behavior of PEGG in positive ion mode. Figures 1A–C show mass spectra from PEGG200 in positive ion mode. Fifteen series of ions, relative to the various ethoxylate oligomers, that differ by $\Delta m/z$ 44 (an ethoxy unit, EO) were observed. Four of them (designated as A–D in Fig. 1A) are PEG oligomers cationized with H^+ , NH_4^+ , Na^+ , and K^+ , and present in the spectrum in high abundance. These adduct ions are clearly detected as the following structures: $[EO_n + H]^+$ ($n = 3–9$, A), $[EO_n + NH_4]^+$ ($n = 6–11$, B), $[EO_n + Na]^+$ ($n = 4–10$, C), $[EO_n + K]^+$ ($n = 4–10$, D). This means that in the first reaction by-products such as PEG-diglucoside and PEG-polyglucosides can be produced, resulting in an excess of PEG. (This was confirmed by the formation of adduct ions of PEG-diglucoside and PEG-polyglucoside in positive ion mode.)

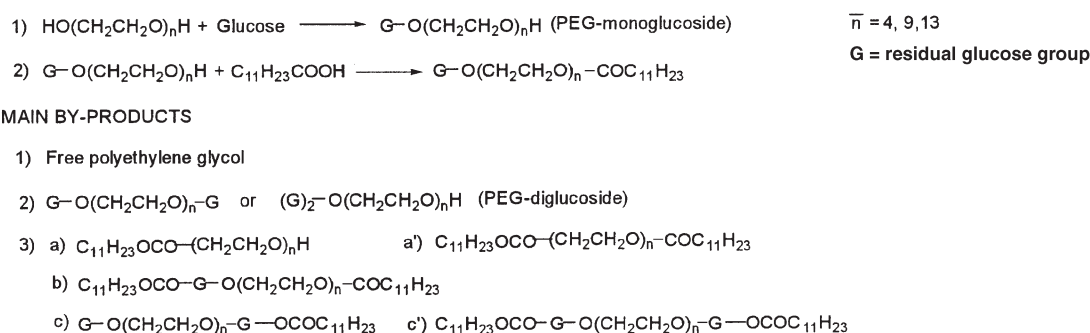
The main products, PEG-monoglucosides were evidenced by four series of cations: $[EO_n G_1 + H]^+$ ($n = 5–6$, E), $[EO_n G_1 + NH_4]^+$ ($n = 5–10$, F), $[EO_n G_1 + Na]^+$ ($n = 3–9$, G), and $[EO_n G_1 + K]^+$ ($n = 4–10$, H) where G_1 is a glucose unit.

There were three additional series of homologous compounds: $[EO_n G_2 + NH_4]^+$ ($n = 4–9$, I), $[EO_n G_2 + Na]^+$ ($n = 4–9$, J) and $[EO_n G_2 + K]^+$ ($n = 4–9$, K), which differ from the F, G, and H series by 162 m/z (a glucose unit), corresponding to the by-product PEG-diglucoside.

Again, in the higher mass range of the spectra, information was observed about PEG-polyglucosides. They can form adducts with NH_4^+ and Na^+ ions: $[EO_n G_3 + NH_4]^+$ ($n = 4–7$, L), $[EO_n G_3 + Na]^+$ ($n = 4–7$, M), $[EO_n G_4 + NH_4]^+$ ($n = 4–6$, N) and $[EO_n G_4 + Na]^+$ ($n = 4–6$, O).

In the lower mass range of the spectra, the ions at m/z 89, 133, and 177 were assigned to $[EO_2 - H_2O + H]^+$, $[EO_3 - H_2O + H]^+$, and $[EO_3 - H_2O + H]^+$ fragments.

In spectra of PEGG200 (Fig. 1), the protonated molecular ions $[M + H]^+$ and $[M + NH_4, K, Na]^+$ adduct ions dominate the mass spectra. The formation of adduct ions $[M + NH_4]^+$ is dependent on the addition of ammonia. Na^+ and K^+ adducts are formed and detected even without the addition of any sodium and potassium salt. These ions can originate from the impurities in the mobile phase and sample. In spite of the fact that H^+ ions were not added, $[M + H]^+$ adducts were present in high abundance. In our opinion, ammonium ions act in part as a proton



SCHEME 2

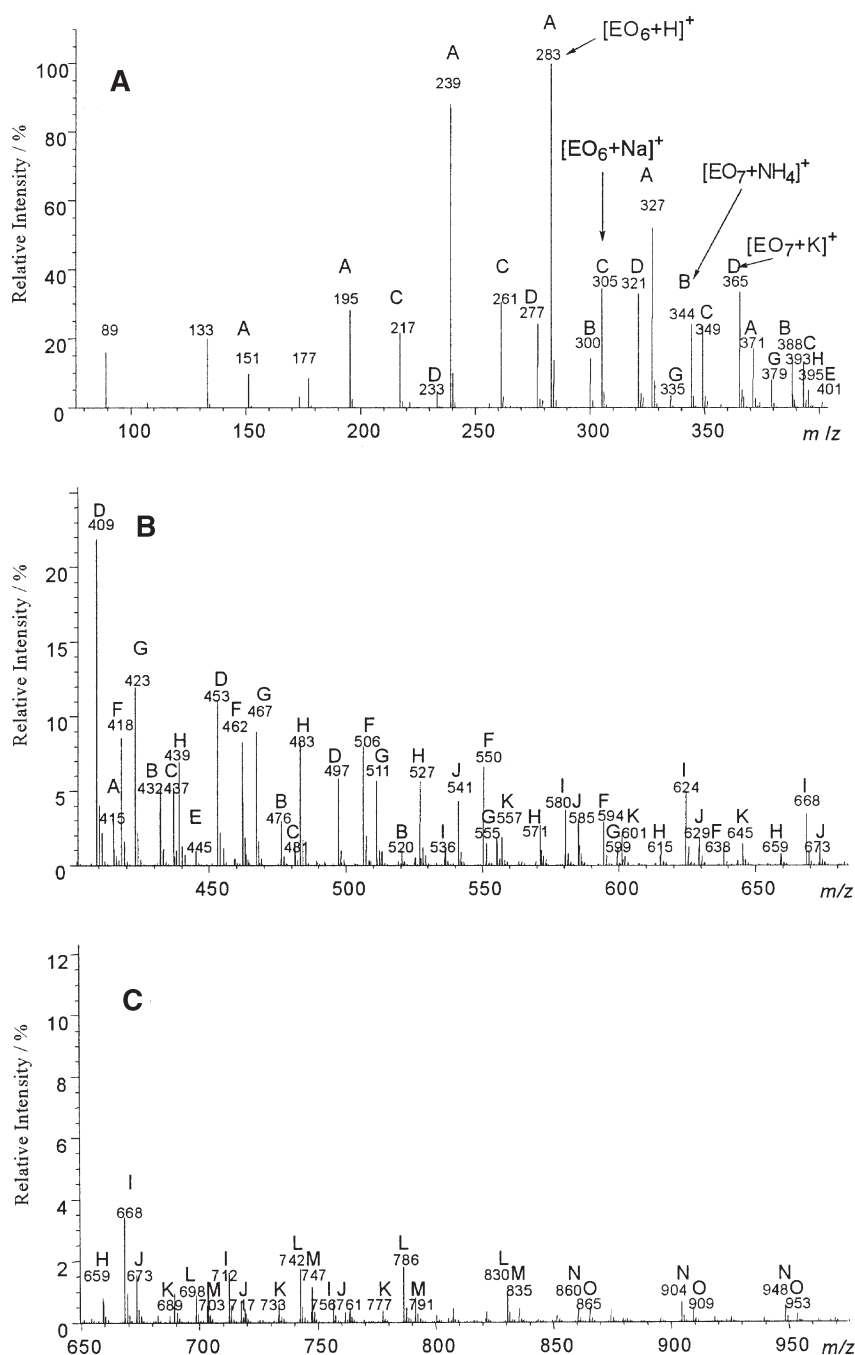


FIG. 1. Atmospheric-pressure ionization MS (API-MS) (positive ion mode) of polyethyleneglycol 200 glucosides (PEGG200).

donor to promote formation of $[M + H]^+$ adducts. In contrast to the abundance of PEG, PEG-monoglucoside and PEG-diglucoside are present in lower abundance in spectra of PEGG200. This can be explained by considering that PEG species have a flexible structure similar to a crown ether, making them capable of forming stable complexes with cations.

Hence, the acetalization product is a multicomponent mixture of starting reactant (PEG), main product (PEG-monoglucoside), and by-products (PEG-diglucoside and -polygluco-

side). The spectra of PEGG400 and PEGG600 registered under the positive ionization mode are displayed, respectively, in Figures 2A and 2B. Their mass spectrometric behavior is similar to that of PEGG200.

Interestingly, the spectra for PEGG200 in Figure 1 show that the ion signal intensities at m/z 283 ($[EO_6 + H]^+$), 305 ($[EO_6 + Na]^+$), 365 ($[EO_7 + K]^+$), and 344 ($[EO_7 + NH_4]^+$) are the strongest for the H^+ , Na^+ , K^+ and NH_4^+ adducts, respectively. However, the manufacturer claims that PEG200 have an average

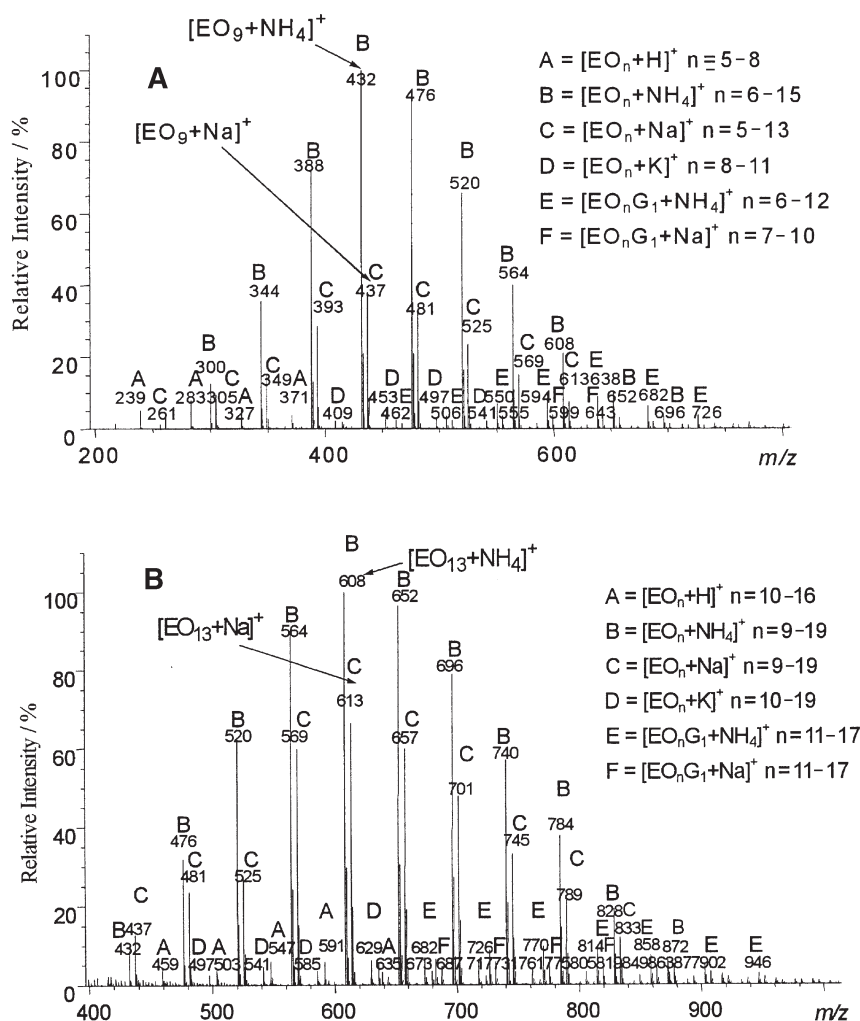


FIG. 2. API-MS (positive ion mode) of PEGG400 (A) and PEGG600 (B). For abbreviations see Figure 1.

of four EO units, which means that the signal intensities of the quasi-molecular ions are distorted. In addition, in the spectra of PEGG400 and -600, the most abundant ions are $[EO_9 + NH_4, Na]^+$ and $[EO_{13} + NH_4, Na]^+$, which correlates well with the manufacturer's claims. This result can be explained by considering that PEG species can form increasingly stable complexes with cations as the n_{EO} increases; after n_{EO} exceeds a critical value of 6 or 7, the increasing trend becomes moderate. The result above can be confirmed by the investigations of Crescenzi *et al.* (11) and Wang *et al.* (12), which described a similar effect of stabilization of cluster ions with cations and aliphatic ethoxylate alcohols (AEO). Figure 3 shows a possible mechanism for the stabilization of charge in the molecule.

API-MS of PEGG-laurate. Figures 4A–C show the positive ion API fingerprint of PEGG200-laurate. Owing to the formation of stable complexes with cations, the most abundant ions are those related to the by-products PEG-mono-laurate and PEG-di-laurate. These adducts have the following structures: $[EO_nR_1 + H]^+$ ($n = 4-7$, A), $[EO_nR_1 + NH_4]^+$ ($n = 4-13$, B),

$[EO_nR_1 + Na]^+$ ($n = 4-7$, C), $[EO_nR_2 + NH_4]^+$ ($n = 3-10$, D) and $[EO_nR_2 + Na]^+$ ($n = 4-7$, E) where R is $C_{11}H_{23}CO-$.

The esterification products of PEGG can be assigned to five series of ions. The following adduct ions belong to PEGG-mono-laurate and by-product PEGG-di-laurate, respectively: $[EO_nG_1R_1 + NH_4]^+$ ($n = 4-8$, F), $[EO_nG_1R_1 + Na]^+$ ($n = 4-6$, G), and $[EO_nG_1R_2 + NH_4]^+$ ($n = 4-8$, H). Two additional series of adduct ions with lower abundance corresponded to the by-products PEG-diglucoside-mono-laurate $[EO_nG_2R_1 + NH_4]^+$ ($n = 4-6$, I) and PEG-diglucoside-di-laurate $[EO_nG_2R_2 + NH_4]^+$ ($n = 4-6$, J).

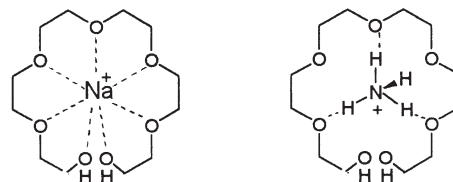


FIG. 3. Structure of stable adduct ions similar to complexes produced by crown ether with cations.

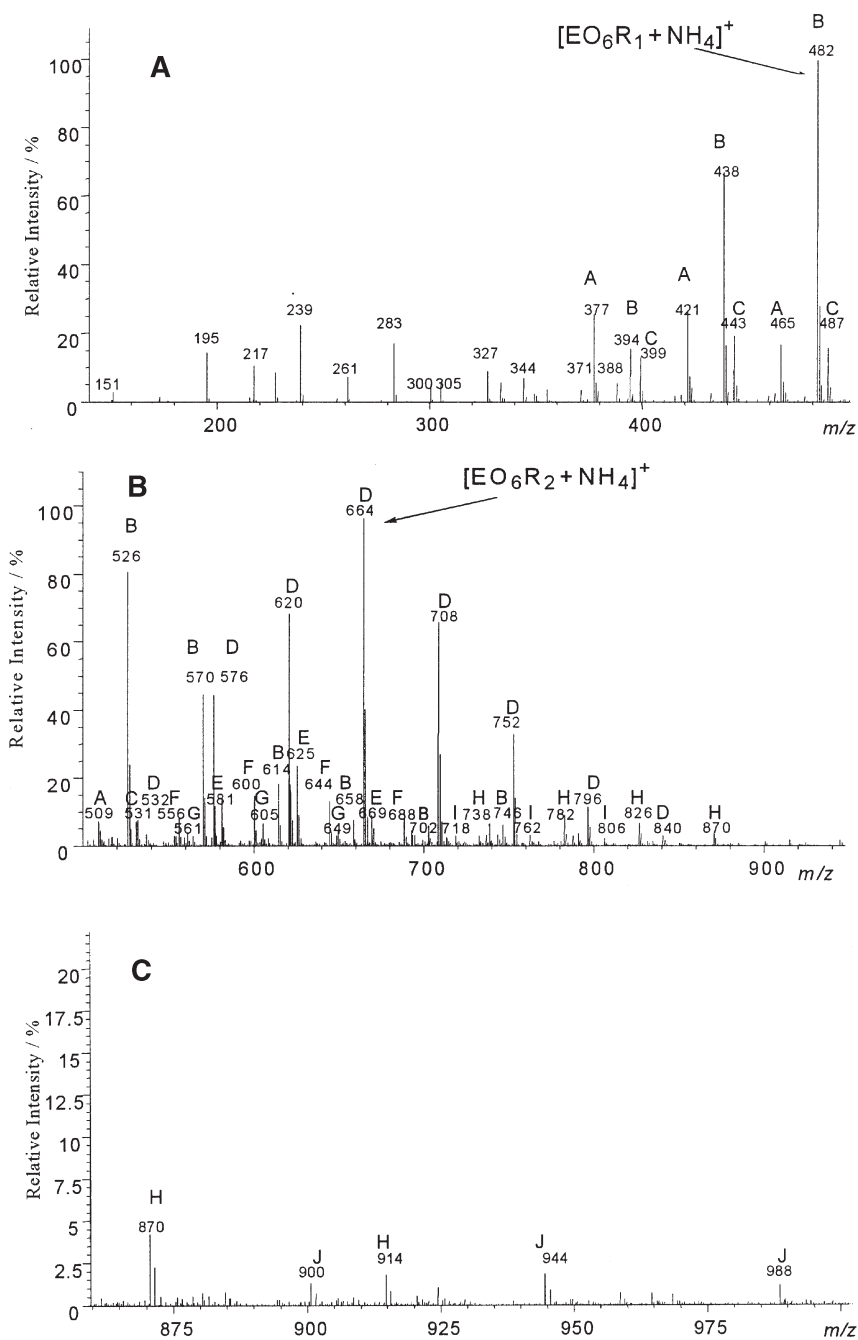


FIG. 4. API-MS (positive ion mode) of PEGG200-laurate. For abbreviations see Figure 1.

In the lower mass range of the spectra unreacted PEG was detected: $[\text{EO}_n + \text{H}]^+$ ($n = 3-8$), ions at m/z 151, 195, 239, 283, 327, 371; $[\text{EO}_n + \text{Na}]^+$ ($n = 4-6$), ions at m/z 217, 261, 305; $[\text{EO}_n + \text{NH}_4]^+$ ($n = 6-8$), ions at m/z 300, 344, 388.

In the spectra the signal intensity of PEG-laurate adduct ions is also distorted, which can be explained by the same reason as in Figure 1. The qualitative composition of the PEGG400- and PEGG600-laurates is similar to that of the PEGG200-laurates, and their spectra registered under positive ionization mode are displayed in Figures 5A and B, respectively.

The above results indicate that API-MS with ESI is simpler and more rapid than chromatographic methods for qualitative analysis of complex surfactant mixtures. Although the presence of more than one signal for each constituent complicated the positive ion mass spectra, due to the formation of adduct ions with different metals, more information about starting materials, final products, and by-products can be obtained. This mass approach is useful for identification of the impurities in the products and in the control of the reaction process.

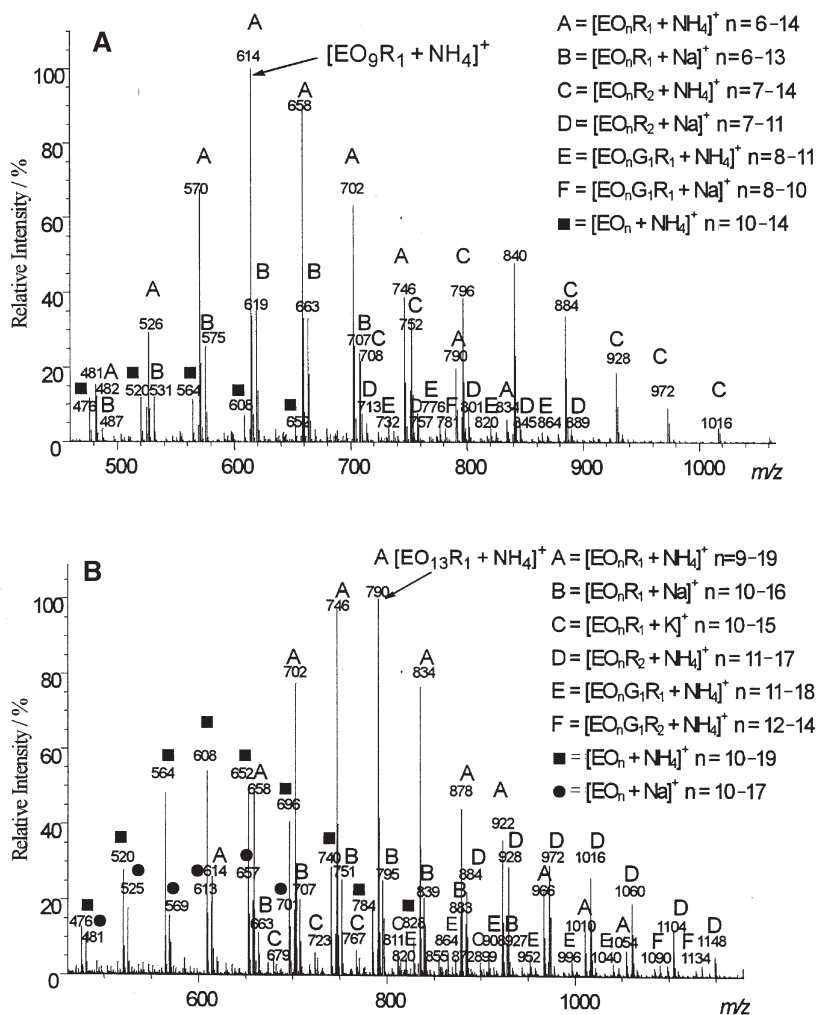


FIG. 5. API-MS (positive ion mode) of PEGG400-laurate (A) and PEGG600-laurate (B). For abbreviations see Figure 1.

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