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ESI-MS studies of polyether surfactant behaviors in reversed-phase HPLC system

Jingke Zhu*, Zuyun Shi

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China

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Abstract

Polyether surfactants were analyzed using liquid chromatography/electrospray ionization-mass spectrometry (HPLC/ESI-MS) with a C_{18} reversed-phase column and a solvent system containing MeOH/H_2O at a flow rate of 500 μL/min. Operating in the positive-ion mode over *m*/*z* 100–900, the sodium and/or proton adduct ions were generated in the ESI interface for alcohol, alkylphenol and amide ethoxylates. MS studies show that conventional RP-HPLC can affect the resolution of most polyether surfactants on the basis of alkyl chain length. Usually, each peak represents a single alkyl chain length but the whole distribution of ethoxy chain lengths with larger alkyl homologs eluting after the smaller ones. Coupled with MS analysis of each peak, a relatively simple RP-HPLC separation is enough to characterize many mixtures of polyether surfactants.

Keywords: Electrospray ionization; RP-HPLC; Polyether surfactants

1. Introduction

Polyethers are synthetic compounds used as non-ionic surfactants in various industry areas worldwide. The materials are generally made by addition of ethylene oxide (EO) to a starting material containing at least one reactive hydrogen, as in the case of fatty alcohols, fatty amides, alkyl phenols, fatty acids and alkyl amines. Most often, the starting materials consist of a range of alkyl chain lengths. The ethylene oxide adds so as to give a Poisson distribution of EO chain length. Therefore, the polyether surfactant commonly occurs as impure mixtures.

For the purposes of characterizing polyether surfactants, the most used approach is HPLC because of its powerful separation ability. The most three frequent HPLC methods are size exclusion [1], RP and normal phase chromatography [2,3]. They are separations on different bases and therefore polyether molecules might show different behaviors in the three modes. The greatest obstacle for HPLC itself to study chromatography behavior of polyether surfactants lies in the lack of standard samples in practice. However, compounds are identified by retention time, hardly a unique characteristic. Choice of a mass spectrometer as a detector allows facile analysis of polyether surfactants, if an electrospray ionization (ESI) interface is applied. In this article, ESI-MS is employed to study the chromatography behavior of polyether surfactants in RP-HPLC mode.

* Corresponding author.
E-mail address: jingkezhu@yahoo.com (J.K. Zhu).

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2. Experimental

2.1. Chemicals

Samples of dodecanol, nonylphenol and octanoyl amide ethoxylates were gifted from Hangzhou Electrochemistry Corp. (Hangzhou, PR China). Methanol was of HPLC grade, and was supplied by Tianjing Reagent Factory (Tianjing, PR China).

Sample solution used for HPLC-MS analysis was prepared by dissolving dodecanol, nonylphenol and octanoyl amide ethoxylates in methanol/water (80:20) as a single solution, which was directly injected for analysis.

2.2. Liquid chromatography-mass spectrometry

Mass spectra were obtained using a Bruker Daltonic Esquire-LC ion trap mass spectrometer equipped with Bruker DataAnalysis system and LC/ESI/MS interface. The mass spectrometer was interfaced to an HP 1100 HPLC system.

LC-MS determinations were performed by operating the mass spectrometer in the positive-ion mode. Mass spectra were acquired over the scan range *m*/*z* 100–900. The nebulizing gas (N_2) was set to 18 psi. Nitrogen drying gas was used at a flow rate of 8 L/min and 300 °C. The ionspray voltage, cap exit offset, skimer 1 and trap drive were 4.0 kV, 77.2, 43.2 and 41.0 V, respectively. Bruker DataAnalysis Esquire-LC 1.6m application version 4.0 was used for data acquisition and processing.

HPLC separation were carried out on an HP ODS Hypersil 125 mm × 4 mm 5 μm column. An isocratic (methanol:H_2O or 0.5% HAc aq. = 80:20) and a 15 min linear gradient from 20:80–90:10 MeOH/H_2O solvent systems were used at a flow rate of 500 μL/min. The mobile phase was delivered by the HP 1100 HPLC system and monitored at 210 nm using a diode-array detector located in-line between the HPLC column and the ESI interface. The data were acquired by HP ChemStation software system using an HP KAYAK XA PC computer.

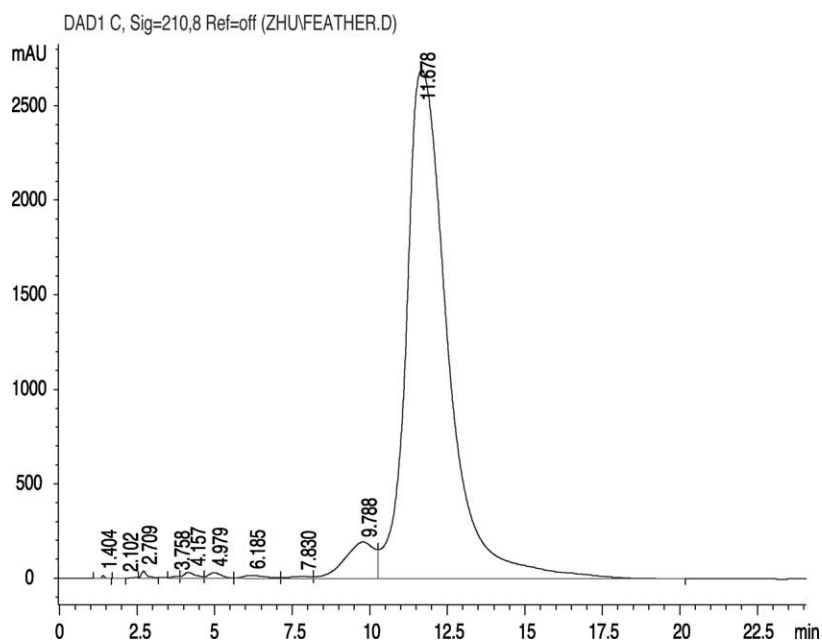


Fig. 1. Chromatogram of polyether surfactants in a non-HAc solvent system.

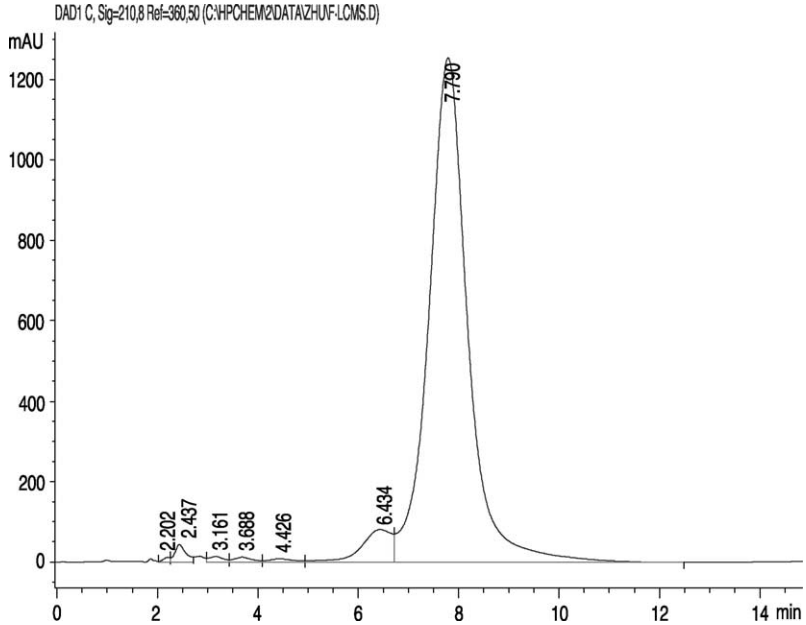


Fig. 2. Chromatogram of polyether surfactants in a solvent system containing 0.1% HAc.

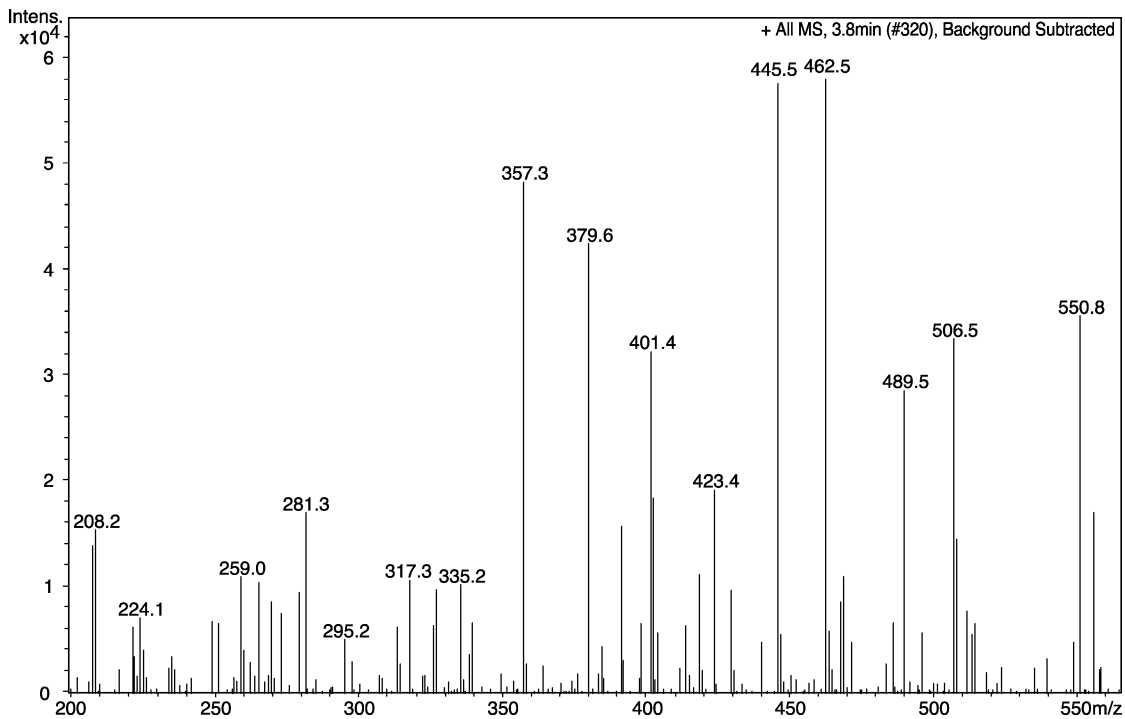


Fig. 3. MS spectrum of 3.8 min peak.

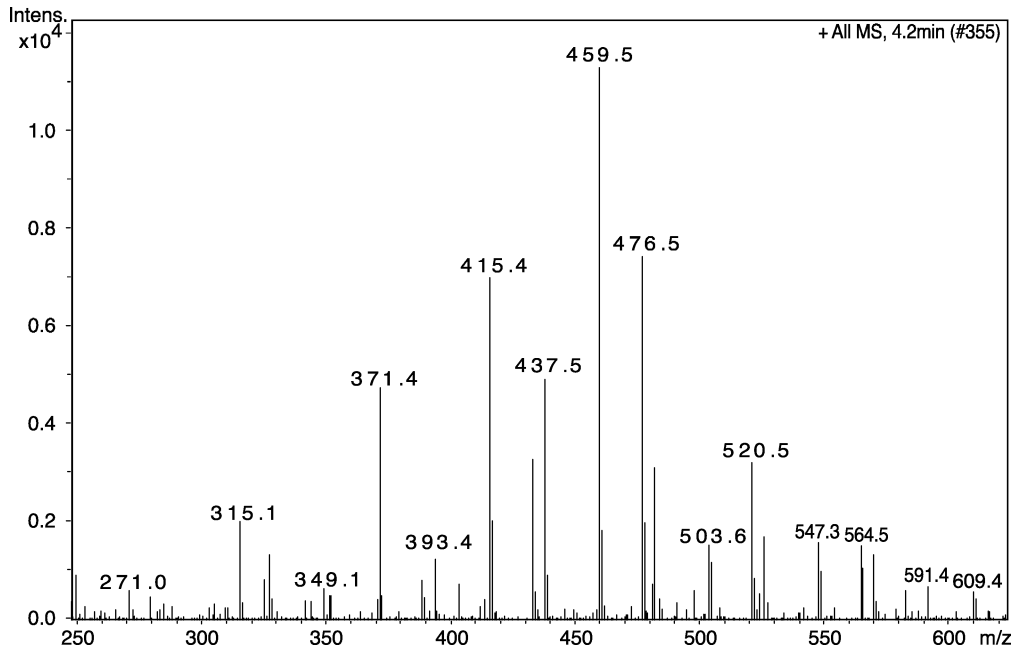


Fig. 4. MS spectrum of 4.2 min peak.

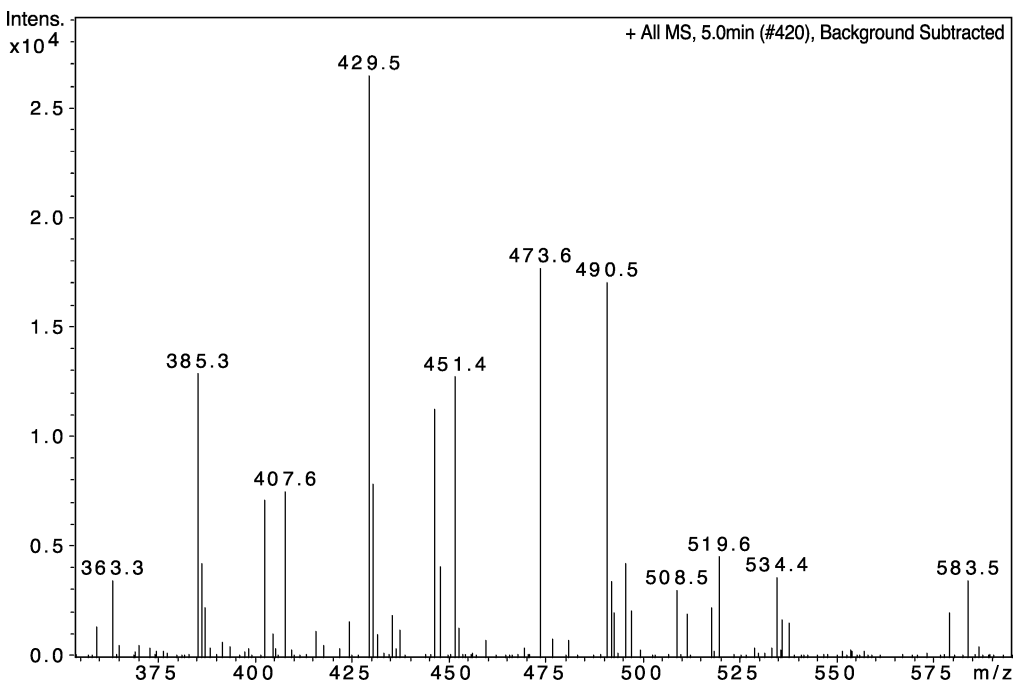


Fig. 5. MS spectrum of 5.0 min peak.

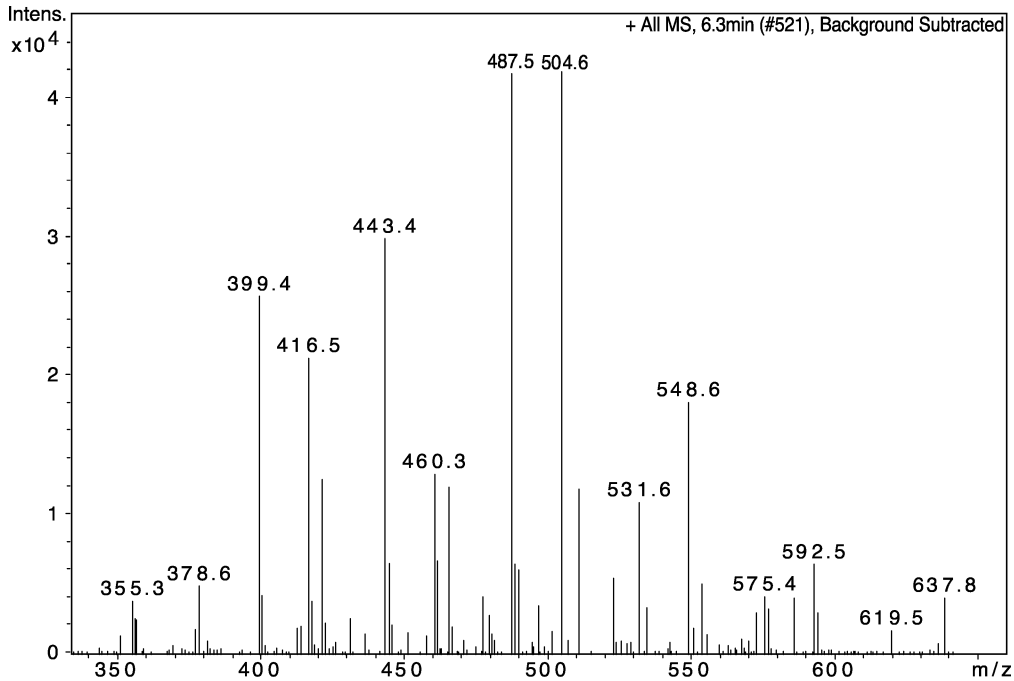


Fig. 6. MS spectrum of 6.3 min peak.

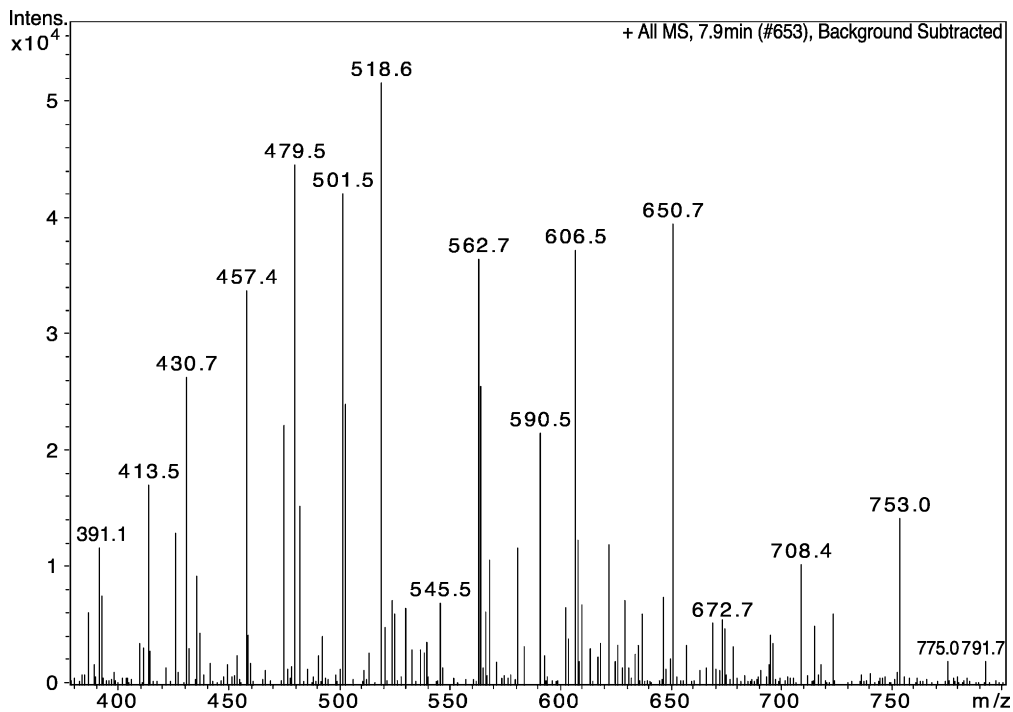


Fig. 7. MS spectrum of 7.9 min peak.

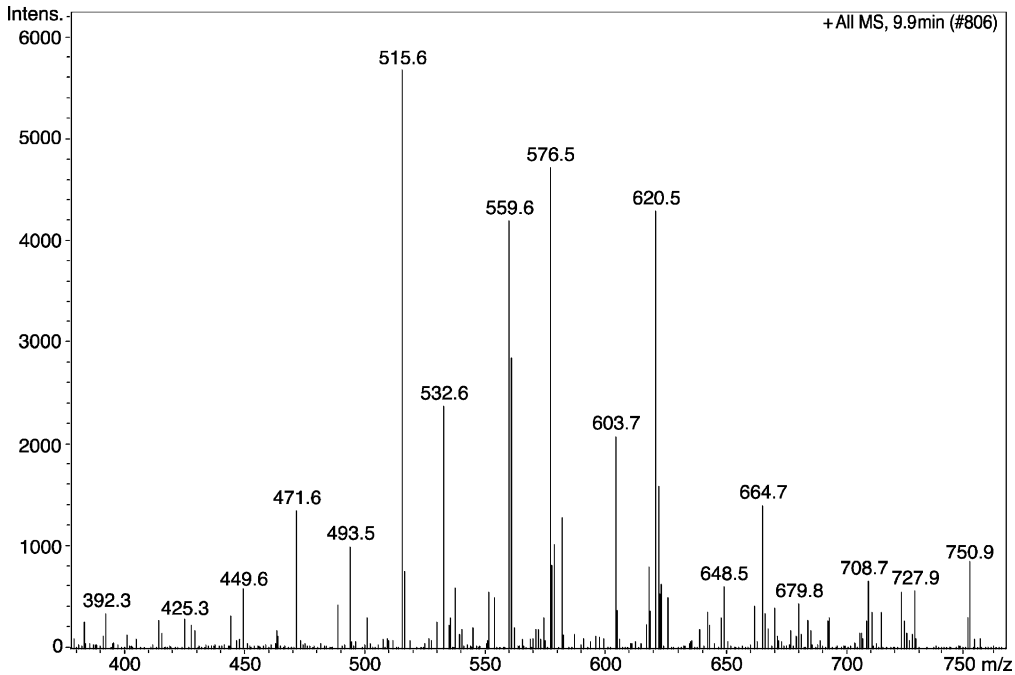


Fig. 8. MS spectrum of 9.9 min peak.

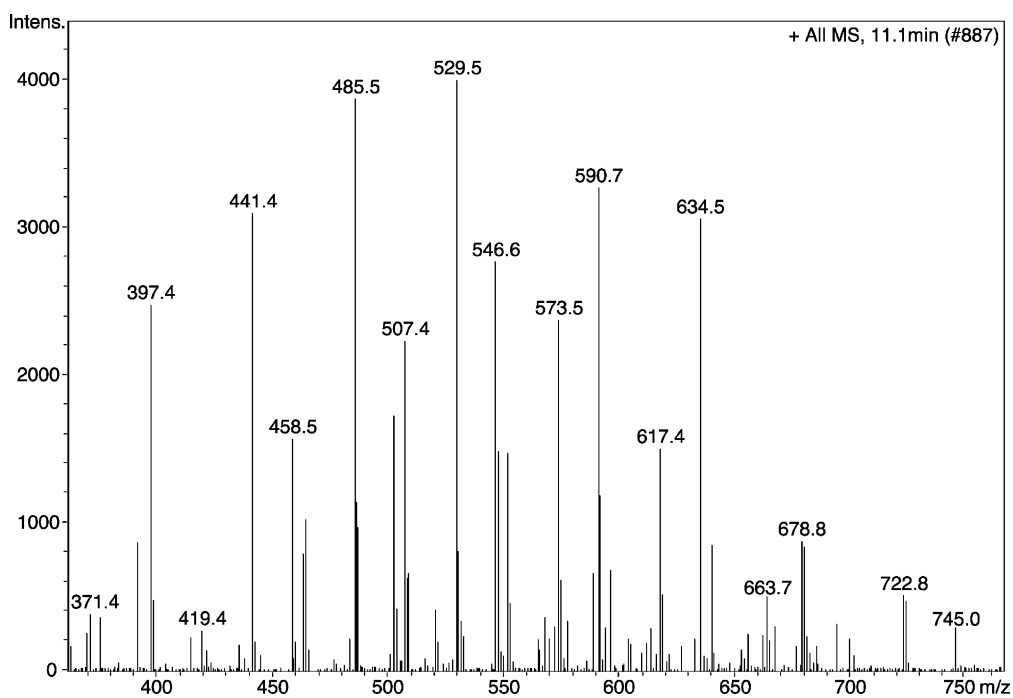


Fig. 9. MS spectrum of 11.1 min peak.

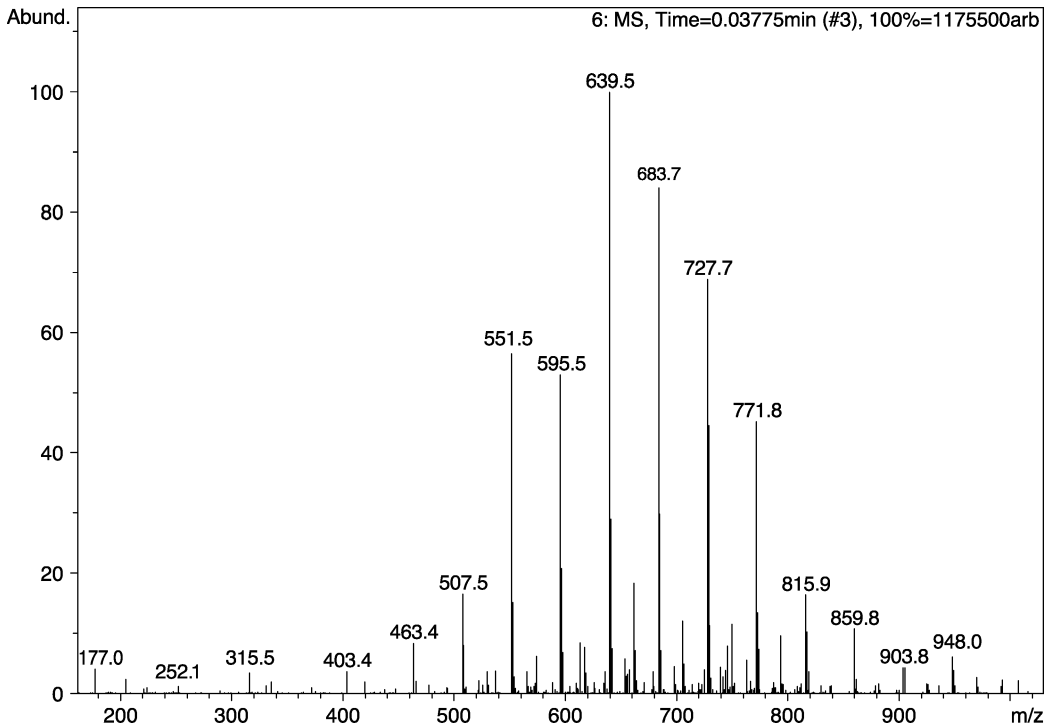


Fig. 10. MS spectrum of nonylphenol ethoxylates.

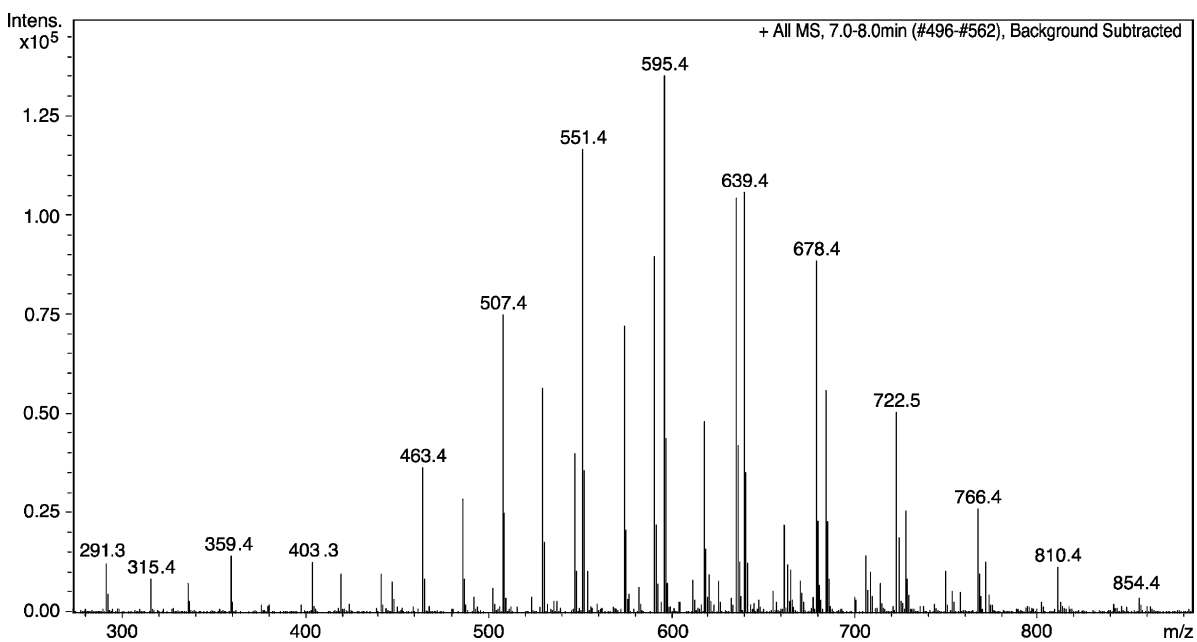


Fig. 11. MS spectrum of 7.7 min peak of the chromatography using 0.1% HAc aq. as solvent.

3. Results and discussions

3.1. HPLC chromatograms and mass spectra of the peaks

Figs. 1 and 2 are the chromatograms of polyether surfactants using CH_3OH/H_2O and CH_3OH/H_2O/HAc as mobile phases, respectively. The recorded mass spectra of the peaks in the chromatography using non-acid solvent system are shown in Figs. 3–9.

3.2. Assignments of compounds in polyether surfactants

In order to investigate the quasimolecular ions generated in ESI, the nonylphenol ethoxylate in CH_3OH/H_2O was introduced into the ESI-MS directly. The MS spectrum (Fig. 10) shows that in a non-acid solvent nonylphenol ethoxylates formed abundant sodiated molecular ions (*m*/*z*: 463, 507, 551, 595, 639, 683, 727, 771, 815, 859) with protonated molecular ions at low abundance (*m*/*z*: 573, 613, 661, 705, 749, 793). According to the results, each peak for the chromatography using non-HAc solvent system was assigned (see Table 1).

3.3. Quasimolecular ions in different solvent systems

As can be seen from Figs. 3–9, the quasimolecular ions are produced and detected for each discrete compound under the given ESI-MS operation conditions. In a non-acid solvent system, polyether surfactants tend to form sodiated molecular ions in ESI interface.

To investigate the quasimolecular ions further, the solvent system was slightly changed by inclusion of 0.1% acetic acid. The chromatogram and the mass spectrum of 7.7 min peak are shown in Figs. 2 and 11, respectively.

Comparison of the mass spectrum obtained using $MeOH/H_2O$ (Fig. 9) with HAc containing solvent (Fig. 11) shows that the abundance of the Gaussian distribution over the ions *m*/*z* 463, 507, 551, 595, 639 683 and 727, which were formerly assigned as $M + Na^+$ ions of nonylphenol ethoxylates in a non-HAc solvent system, was significantly enhanced. This abundance enhancement is considered a contribution by protonated molecular ions of hexadecanol ethoxylates (*m*/*z* 463, 507, 551, 595, 639 683 and 727) owing to the existence of HAc. The result indicates that alcohol ethoxylyates tend to form $M + H^+$ ions in a solvent containing HAc. On the other hand, the sodiated molecular ions of amide ethoxylates (*m*/*z*: 502, 546, 590, 634, 678, 722, 766, 810, 854) dominate in both solvent systems (Figs. 9 and 11), which indicates that HAc has little effect on the amide ethoxylate quasimolecular ions generated in ESI.

3.4. Behaviors of polyether surfactants in different solvent systems

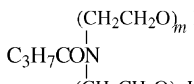
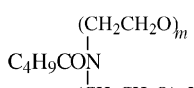
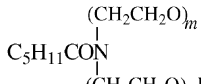
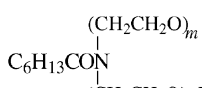
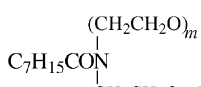
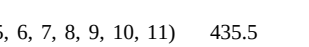
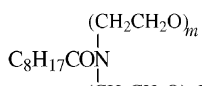
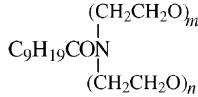
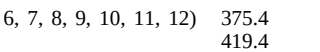
It can be seen from the assignments (Table 1) that each peak usually represents a single alkyl chain length but the whole distribution of ethoxy chain lengths in an isocratic $MeOH/H_2O$ solvent system. Although the retention time for each surfactant compound was shortened in a 0.1% HAc containing $MeOH/H_2O$ solvent system (see Fig. 2), separation of polyether surfactants was achieved by alkyl chain length too (see Fig. 11).

During gradient run, the separation based on alkyl chain length, with baseline drift, was observed in the study. Although no quantitative analyses were carried out, it is still a potential tool for HPLC to determine polyether surfactants quantitatively. Adding complexity by drifting the baseline, the gradient is to be avoided in quantitative analysis whenever possible.

The results obtained indicate that conventional RP-HPLC can affect the resolution of most polyether surfactants on the basis of alkyl chain length with larger alkyl homologs eluting after the smaller ones. In the case of a product made by ethoxylation of a broadly distributed hydrophobe, retention time of lower ethoxylation of higher molecular weight hydrophobes may overlap with those of lighter ethoxlates of lower molecular weight hydrophobes so that resolution is impossible.

LC-MS studies show that RP-HPLC alone is insufficient to determine ethoxy chain length for polyether

Table 1
Peak assignments

R_t (min)	m/z ($M + Na^+$)	Assignment	m/z ($M + Na^+$)	Assignment	m/z ($M + Na^+$)	Assignment
3.8	375.3 401.4 445.5 489.5	$C_{10}H_{21}O(CH_2CH_2O)_nH$ (n: 4, 5, 6, 7)	418.4 462.5 506.5 550.8		335.2 379.6 423.4	 (n: 4, 5, 6)
4.2	371.4 415.4 459.5 503.6	$C_{11}H_{23}O(CH_2CH_2O)_nH$ (n: 4, 5, 6, 7)	432.3 476.5 520.5 564.5		349.1 393.4 437.5 481.5 525.4	 (n: 4, 5, 6, 7, 8)
5.0	385.3 429.5 473.6 517.6	$C_{12}H_{25}O(CH_2CH_2O)_nH$ (n: 3, 4, 5, 6)	402.4 446.5 490.5 534.6		363.3 407.6 451.4	 (n: 4, 5, 6)
6.3	399.4 443.4 487.5 531.6 575.4 619.5	$C_{13}H_{27}O(CH_2CH_2O)_nH$ (n: 4, 5, 6, 7, 8, 9)	416.5 460.3 504.6 548.6 592.5		421.5 465.4 509.6	 (n: 5, 6, 7)
7.9	413.5 457.4 501.5 545.5	$C_{14}H_{29}O(CH_2CH_2O)_nH$ (n: 4, 5, 6, 7)	386.5 430.7 474.5 518.6 562.7 606.5 650.7		435.5 479.5 523.5	 (n: 5, 6, 7)
9.9	471.6 515.6 559.6 603.7	$C_{15}H_{31}O(CH_2CH_2O)_nH$ (n: 5, 6, 7, 8)	532.6 576.5 620.5 664.7 708.4		449.6 493.5	 (n: 5, 6)
11.1	397.4 441.4 485.5 529.5 573.5 617.4 661.4	$C_{16}H_{33}O(CH_2CH_2O)_nH$ (n: 3, 4, 5, 6, 7, 8, 9)	458.5 502.5 546.6 590.7 634.5 678.8 722.8		375.4 419.4 463.4 507.4 551.5 595.4 639.5	 (n: 3, 4, 5, 6, 7, 8, 9)

surfactants. If an ESI interface is applied, which permits direct introduction of the effluent of the LC into the MS, provides a very selective detector and gives additional information, so that the RP-HPLC is not required to separate both by degree of ethoxylation and by the alkyl moiety.

4. Conclusion

Positive ESI-MS may be used for polyether surfactant analysis, and sodiated and/or protonated molecular ions were generated for all the polyether surfactants investigated. LC/ESI-MS is compatible with MeOH/H_2O or MeOH/H_2O/HAc solvents used during C_{18} reversed-phase HPLC.

MS studies show that separation of polyether surfactants is based on the alkyl chain length in a conventional reversed phase HPLC, which indicates that RP-HPLC itself is not adequate to determine ethoxy chain length. By coupling RP-HPLC with MS, quasimolecular ions were produced for each discrete compound, so that a relative simple HPLC separation is enough to characterize many mixtures of polyether surfactants.

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