

The Fragmentation of Ethoxylated Surfactants by AP-MALDI-QIT

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Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry is an important technique to characterize synthetic polymers. MALDI mass spectral data is used to determine the polymer average molecular weights, repeat units, and end groups. The development of atmospheric pressure (AP) sources for MALDI has enabled the interface of MALDI ion sources with a variety of mass spectrometers. Using AP-MALDI we have investigated the fragmentation of ethoxylated (EO) surfactants in a quadrupole ion trap (QIT) via collision induced dissociation (CID).

We have analyzed a variety of telomers of low molecular weight, ethoxylated surfactants. The majority of the study examined telomers of Surfynol⁷ surfactants. The Surfynol backbone is 2,4,7,9-tetramethyl-5-decyne-4,7-diol. The samples were prepared with the same methods developed for vacuum MALDI. We found that AP-MALDI produced essentially the same mass spectra as we have previously observed using vacuum MALDI for these nonionic ethoxylated surfactants. The Surfynol surfactants were prepared using methanol as the solvent and 2,5-dihydroxybenzoic acid (DHB) as the matrix. Na, K, and Li-cationized oligomers were studied. The experiments were done on an Agilent 1100 LC/MSD Ion Trap SL AP-MALDI-QIT instrument. MS² and MS³ mass spectra were compared to previous MALDI-PSD experiments [Hanton and Parees 2002 ASMS Poster].

MS, MS², and where possible, MS³ mass spectra for a variety of telomers of ethoxylated Surfynol surfactants were collected. Figure 1 shows an example of the MS² mass spectrum of the predominantly n = 23 telomer of Surfynol 4XX. We see three main fragmentation paths. Two of these paths are identical to the MALDI-PSD results.

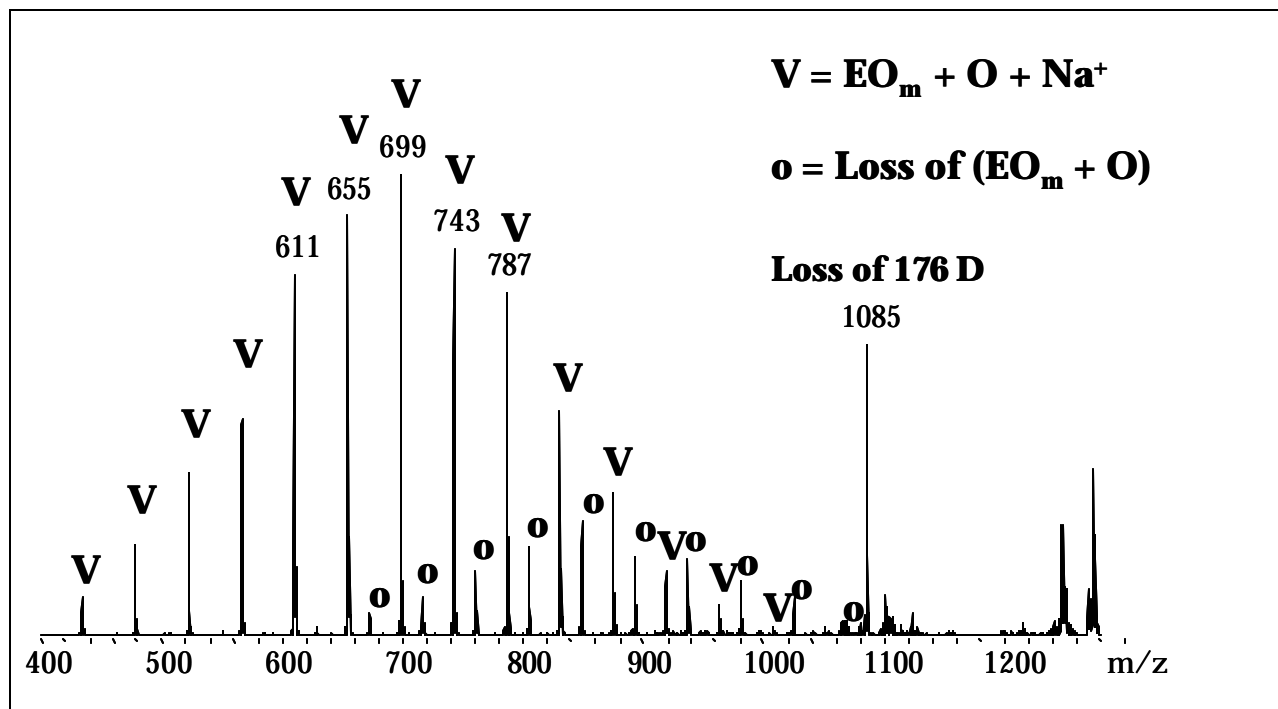


Figure 1: AP-MALDI-QIT MS² mass spectrum of the n=23 telomer of Surfynol 4XX

The main fragmentation path (?) is assigned as the loss of the hydrophobe backbone of the surfactant. The minor fragmentation path (?) is assigned as the loss of EO units from the end of the surfactant. The main difference from the PSD mass spectrum is the presence of the -176 D fragment ion. This ion is assigned as the loss of a NaDHB matrix adduct and indicates that the precursor ion, m/z 1262, is a mixture of $n = 23$ and ($n = 19 + \text{NaDHB}$). The matrix adduct ion is in the mass window because NaDHB has the same nominal mass as four EO units, 176 D. In the PSD experiments, an unassigned fragment ion was observed at -161 D. Perhaps these are the same ions, but the matrix adduct ion fragments promptly in the PSD experiment and is not properly mass identified by PSD. The high efficiency of this fragmentation may also account for its disproportionately strong signal intensity in both the PSD and CID experiments.

Figure 2 shows the MS^3 mass spectrum of the 1085 D fragment ion from the ($n = 19 + \text{NaDHB}$) adduct telomer of the Surfynol surfactant ion at m/z 1262 observed in Figure 1. In this mass spectrum we can clearly see the same fragments observed above. These data demonstrate that the 1085 D fragment ion is also an ethoxylated Surfynol S4XX telomer. We can even observe a low intensity ion at -176 D, m/z 909 that is assigned as the loss of a second NaDHB matrix adduct. This indicates that the original precursor at m/z 1262 was actually a mixture. The predominant species is the $n = 23$ S4XX telomer, but the signal also contained contributions from the ($n = 19 + \text{NaDHB}$) and ($n = 15 + 2 \text{NaDHB}$) telomers.

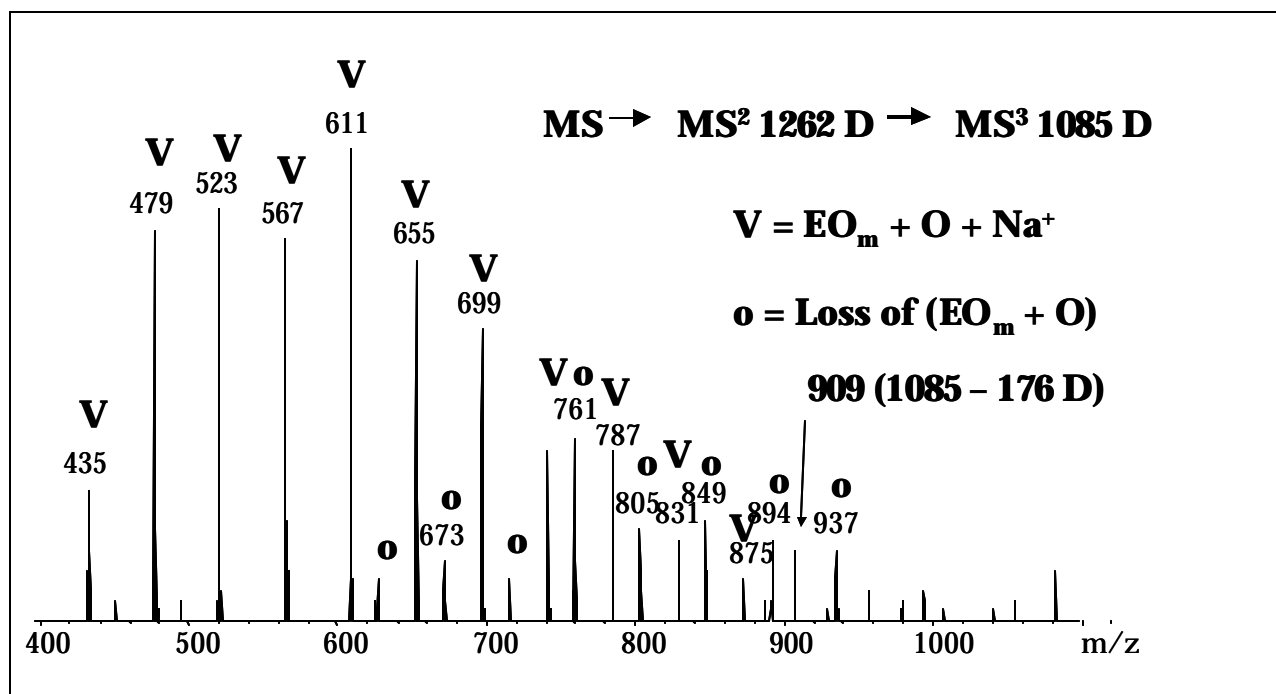


Figure 2: AP-MALDI-QIT MS^3 mass spectrum of the $n=23$ telomer of Surfynol 4XX

Further experiments using different cations show that NaDHB matrix adducts are formed even with addition of Li and K salts as cationization agents. The MS^2 experiments show the loss of 160 and 192 D fragments which are assigned as LiDHB and KDHB matrix adducts. MS^3 experiments on the fragments from these adducts, however, show Na-cationized fragment ions, similar to those observed above in Figure 2. Of course, a Na atom and a DHB molecule are required for the adduct to have the proper mass for the fragmentation mass window. It is interesting that the Li or K cation is lost as a matrix adduct during MS^2 . The Na cation appears to be preferentially associated with the telomers of the Surfynol surfactant.