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Characterization of synthetic and commercial trisiloxane surfactant materials

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The organosilicone surfactant Silwet L-77® (L-77), used as an agrochemical adjuvant, is a mixture comprised predominantly of $[(CH_3)_3SiO]_2-(CH_3)Si-(CH_2)_3-(OCH_2CH_2)_n-OCH_3$ oligomers ($n = 3$–16, average $n \approx 7.5$). The commercially available L-77 mixture was purified by reversed-phase high-performance liquid chromatography (HPLC) to obtain individual trisiloxane surfactant components. Pure oligomers ($n = 3$, 6 and 9) were also synthesized. Synthesis was achieved by hydrosilylation of monomeric ethoxylate monomethyl ether starting reagents. Pure hexa- and nona-ethylene glycols were produced by condensation of smaller oligomers.

Atmospheric-pressure ionization mass spectrometry (MS) methods were used to characterize fully the commercial L-77 product and synthesized or isolated components. The application of Fourier-transform ion cyclotron resonance MS and online HPLC–electrospray ionization MS techniques to the analysis of this surfactant are described here. The application of these analytical techniques also enabled elucidation of the synthetic by-products present in the commercial formulation.

In addition, physico-chemical properties specific to agrochemical uses, such as droplet spread areas on plant foliage and surface tension for the different oligomer solutions, are also reported. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organosilicone surfactant; Silwet L-77®; trisiloxane surfactant; atmospheric-pressure chemical ionization mass spectrometry; physical properties

INTRODUCTION

Surfactants are commonly used in agrochemical formulations as adjuvants to improve physico-chemical characteristics of the spray solution and to increase the uptake of active ingredients into plants or target organisms.[1–3] The use of organosilicone surfactants in agrochemical applications is becoming increasingly widespread,[4] with the trisiloxane-based derivatives the most commonly used. The enhancement of the efficacy of active ingredients in the field by these surfactants has been related to their 'superspreading',[5] especially in the case of stomatal infiltration mechanisms.[6]

In this paper we report the results of an extensive characterization of a commercially available trisiloxane surfactant, Silwet L-77® (L-77), and some of the individual representative oligomers. L-77 (1) is an oligomeric mixture of trisiloxy polyethoxylate monomethyl ethers, $[(CH_3)_3SiO]_2-(CH_3)Si-(CH_2)_3-(OCH_2CH_2)_n-OCH_3$ (average $n = 7.5$). For convenience, these will be abbreviated to $M_2D-C_3-O-(EO)_n-Me$ hereafter (where $M = (CH_3)_3-Si-O_{(0.5)}-$, $D = O_{(0.5)}-Si(CH_3)-O_{(0.5)}$ and $EO = CH_2CH_2O$). The objective was to characterize the commercial product and individual components, in order to provide an understanding of the relative influence and mode of action of these oligomers individually, and in the combined (commercial) product. Novel synthetic approaches and analytical methods were investigated; in addition, physico-chemical properties such as droplet spread on plant foliage and surface tension of the bulk solutions were also determined.

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Different methods were used to provide pure oligomers, including synthesis and preparative high-performance liquid chromatography (HPLC) of the commercial surfactant product.

A further aim of this research was the novel application of atmospheric-pressure ionization mass spectrometry (API-MS) methods to the analysis of this product. Traditionally, size-exclusion chromatography (SEC),[7] nuclear magnetic resonance (NMR),[8] and Fourier transform infrared (FT-IR) spectroscopy[9] have been common methods for the analysis of silicones and silicone polyether copolymers.[10] Gas chromatography (GC)–MS methods have also been applied to the quantification of silicone polyether copolymer constituents. However, the higher molecular weight oligomers could not be detected, even following derivatization;[11] furthermore, high fragmentation of siloxanes under conventional electron impact (EI) MS detection results in limited parent molecule information.[12] The observation of common rearrangement products for different structures (e.g. cyclic siloxanes and linear silanols)[13] also presents limitations in the application of GC–MS for structural elucidation purposes.

Conventional HPLC detection techniques are generally not suitable for organosilicone compounds, due to the lack of ultraviolet (UV)-sensitive chromophores in the molecules, lack of specificity and insufficient sensitivity. HPLC with evaporative light scattering mass detection (ELSD) has been used,[14] but low concentrations or lower molecular weight oligomers could not be detected by this technique.[15,16] The detection of trisiloxane surfactants and selected degradation products, by HPLC online with inductively coupled plasma atomic emission spectroscopy (ICP-AES), has also been described, although no experimental data were published.[17] Matrix-assisted laser desorption ionization (MALDI) MS following HPLC has also been reported,[18] though the difference in the sample phase for these techniques (solid versus liquid) precludes online coupling. Furthermore, mass discrimination at low molar mass ranges (<1000 amu) has been described for MALDI methods, and remains a potential limitation in data interpretation.[19,20]

Atmospheric-pressure chemical ionization (APCI) and electrospray ionization (ESI) techniques, coupled with MS, are extremely attractive analytical methods. They provide specific and selective detection, potentially to very low levels, with the added ability to analyse online following HPLC separation techniques. These API-MS methods have been successfully applied to the analysis of ionic and nonionic surfactants, with surface-active compounds often giving very high responses with ESI due to the nature of the ionization process.[21–23] The aim of this work was to apply, for the first time, the API-MS method to the analysis of trisiloxane surfactants, and to demonstrate the validity of the technique for their structural characterization.

METHODS AND MATERIALS

HPLC

Three Waters Delta-Pak (25 mm × 100 mm, 15 µm, 100 Å, octadecyl (C_{18})) modified reversed-phase (RP) Radial-Pak columns were used in series with detection by refractive index (RI) for preparative HPLC work.

Semi-preparative HPLC was with an Ultrasphere ODS C_{18} column (Beckman, 10 mm × 250 mm, 5 µm) with an elution solvent of $35:65$ $H_2O:CH_3CN$, and a flow rate of 3 ml min^{-1}; the eluant was divided post-column to deliver 0.5 ml min^{-1} to the evaporative light scattering mass detector and 2.5 ml to the fraction collector.

Analytical analyses were performed on an RP C_{18} column (Phenomenex, 4.6 mm × 150 mm, 3 µm) with an elution solvent of $30:70$ $H_2O:CH_3CN$ (0.5 ml min^{-1}). A split of 0.05 ml min^{-1} to the detector was used for detection by ESI-MS.

Routine HPLC–ELSD was performed using a Biorad Model AS-100 automatic sampler, Rheodyne injector, and Hewlett Packard Model 1050 pump, operated isocratically. Detection was with a Varex ELSD Mk III (nebulizer gas: air; flowrate: 2.4 l min^{-1}; evaporator tube temperature: 100 °C), equipped with a Hewlett Packard 3396A integrator to measure peak areas.

API-MS

Analyses were performed with a single quadrupole VG Platform II mass spectrometer (Fisons/Micromass), equipped with ESI and APCI interfaces, utilizing MassLynx 2.0 software. Samples (1 ppm) were injected manually with a Rheodyne Model 7125 injector (10 µl loop) and mobile phase was delivered by a Spectra System P1000 isocratic pump (Spectra-Physics Analytical). Analyses were performed in total ion mode (TIC; m/z range: 300–1000; scan time: 4 s; inter-scan time: 0.1 s; eluant: $1:2$ $H_2O:MeOH$) unless stated otherwise. The ESI-MS conditions were: capillary, 4.2 kV; cone voltage, 60 V; solvent, 0.02 ml min^{-1}; drying gas, 200 l h^{-1}. The conditions altered for HPLC–ESI-MS were: solvent, 0.3 ml min^{-1}; drying gas, 300 l h^{-1}; source, 180 °C. The APCI-MS conditions were: corona, 1.6 kV; cone voltage, 60 V; solvent, 1 ml min^{-1}; drying gas, 100 l h^{-1}; sheath gas, 250 l h^{-1}; probe, 300 °C; source, 180 °C.

Fourier-transform ion cyclotron resonance (FTICR)-MS spectra were obtained using a Spectrospin CM-47 FTICR, equipped with a cylindrical ICR cell (radius 30 mm × 60 mm in length) within a 4.7 T superconducting magnet (Bruker). All samples (0.1 mg ml^{-1}, MeOH) were infused directly via a syringe pump, with 0.1 mg ml^{-1} of NaI added to facilitate ionization. For ESI measurements the instrument settings were: capillary, 1 kV; drying gas, 10 l h^{-1}; heater, 250–300 °C; solvent, 1 µl min^{-1}. For APCI, the settings were: cylinder, 1.3–1.4 kV; end plate, 2.5 kV; capillary, 2.8 kV; drying gas, 5 l h^{-1}, 200 °C; needle sheath gas, 60 l h^{-1}; APCI heater, 200–350 °C; solvent, 0.2–1 ml min^{-1}.

NMR spectroscopy

^{1}H NMR spectra were acquired with samples prepared in $CDCl_3$ or D_2O on a Bruker DRX400 instrument, using an observation frequency of 400.13 MHz.

Chemicals

L-77, Silwet® 408, and $[Si(CH_3)_3{-}O{-}]_2{-}SiH(CH_3)$ were obtained from Crompton Corporation, Organosilicones Group, Tarrytown, NY. Polyethers were used as supplied by Aldrich. Other chemicals used were at least of reagent grade.

Isolation of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ from L-77

A purified sample of the $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ components of L-77 was obtained by preparative RP C_{18} HPLC (50 mg, 500 µl injection aliquots) using an elution solvent of 15:85 $H_2O:CH_3CN$ at a flow rate of 10 ml min^{-1}.

Pure individual oligomers of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ products ($n = 6{-}15$) were obtained by RP C_{18} gravity elution and HPLC of the commercially available product. The L-77 (115 mg) was purified by RP C_{18} gravity elution column chromatography (5 cm × 3 cm i.d., 50% aqueous MeOH to 100% MeOH), followed by semi-preparative RP C_{18} HPLC-LSD equipped with a zero-volume solvent splitter to allow simultaneous detection and fraction collection. Fractions were concentrated by a combination of rotary evaporation, vacuum, and freeze-drying methods.

Synthesis of $M_2D{-}C_3{-}O{-}(EO)_n$ Me siloxanes

Pure $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ ($n = 3$, 6 and 9) oligomers were synthesized by reaction of allyl-capped oligoethoxylate monomethyl ethers with bis(trimethylsiloxymethylsilane) $\{M_2D^H, [(CH_3)_3Si{-}O{-}]_2{-}SiH(CH_3)\}$ over a platinum catalyst (Scheme 1). The allyl-capped ethoxylate monomethyl ethers were synthesized by reaction of allyl chloride with the corresponding ethoxylate monomethyl ethers. The resulting trisiloxane alkylethoxylate products were purified by chromatographic methods and characterized by GC–MS and API-MS.

Allylation of the oligoethylene monomethyl ethers

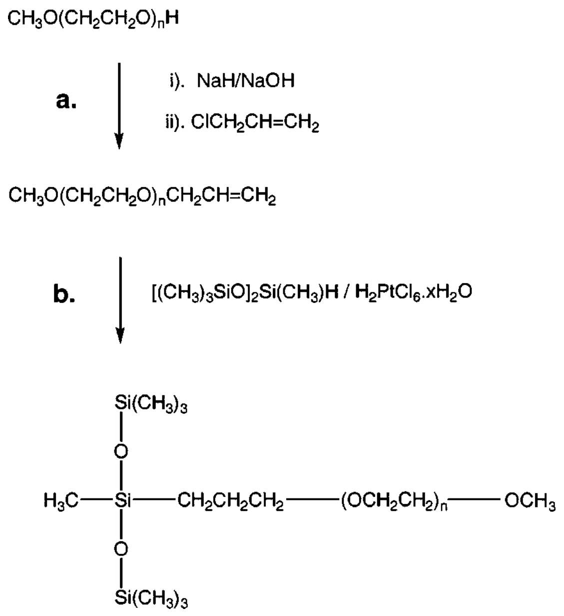
The alkoxide ion of $CH_3O(CH_2CH_2O)_3H$ (10.02 g, 0.06 mol) was generated with NaH (4.39 g, 0.18 mol) by reflux in tetrahydrofuran (THF) for 3 h (nitrogen, stirring). Addition of $ClCH_2CH{=}CH_2$ (5 ml, 0.09 mol) followed by a 2.5 h reflux gave $CH_3O(CH_2CH_2O)_3CH_2CH{=}CH_2$ as a yellow oil at a yield of 85% (10.65 g), following purification by filtration (Scheme 1, step **a**).

The alkylation procedure for the $n = 6$ and 9 ethoxylate monomethyl ethers was varied only in that NaOH rather than NaH was used, NaOH being preferred for safety reasons.

Hydrosilylation of alkyloligoethylene monomethyl ethers

The hydrosilylation (Scheme 1, step **b**) of $CH_3O(CH_2CH_2O)_3$ $CH_2CH{=}CH_2$ (10.65 g, 0.05 mol) with M_2D^H (11.62 g, 0.05 mol) was achieved with the catalyst $H_2PtCl_6{\cdot}xH_2O$ under reflux (3.5 h, THF).[24] The $M_2D{-}C_3{-}O{-}(EO)_3{-}Me$ product was purified via normal-phase SiO_2 chromatography (100% heptane → EtOAc → 100% CH_3CN) at 81% yield (18.06 g) for the hydrosilylation reaction, giving an overall synthetic yield of 69%. A portion of the product was further purified by semi-preparative RP C_{18} HPLC with 90:10 $MeOH:H_2O$ as the elution solvent. The purity of the resulting fraction was greater than 95%, as determined by analytical RP C_{18} HPLC (85:25 $MeCN:H_2O$, 1 ml min^{-1}) and GC–MS.

The overall reaction yield obtained for the $M_2D{-}C_3{-}O{-}(EO)_6{-}Me$ oligomer was 37%, at a purity of 96% (4% contribution from $M_2D{-}C_3{-}O{-}(EO)_5{-}Me$). This synthetic procedure yielded 90% pure $M_2D{-}C_3{-}O{-}(EO)_9{-}Me$ (6% and 4% contribution from the $(EO)_8$ and $(EO)_7$ oligomers respectively), at a reaction yield of 0.8%.



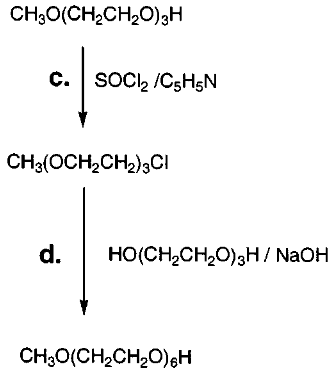
Scheme 1. Reaction sequence adopted to yield trisiloxane alkylethoxylate (**1**) oligomers.

Preparation of the oligoethyleneglycol monomethyl ethers

The longer chain oligoethyleneglycols ($n = 6$ and 9) were produced by combination of smaller oligomers, following a modified method from Krespan[25] involving etherifications and chlorinations.

Synthesis of $HO{-}(EO)_6{-}Me$

The method used for preparation of $HO{-}(EO)_6{-}Me$ is shown in Scheme 2. The chlorination of $CH_3O(CH_2CH_2O)_3H$ (10 ml, 0.06 mol) with $SOCl_2$ (14 ml, 0.19 mol) to form $CH_3(OCH_2CH_2)_3Cl$ was achieved by catalysis with pyridine under reflux (nitrogen, stirring, 4 h), step **c**. The concentrated $CH_3(OCH_2CH_2)_3Cl$ was then etherified with $HO(CH_2CH_2O)_3H$ (17 ml, 0.12 mol) in the presence of NaOH (4.94 g, 0.12 mol) at 130 °C (nitrogen, stirring, 10 h), step

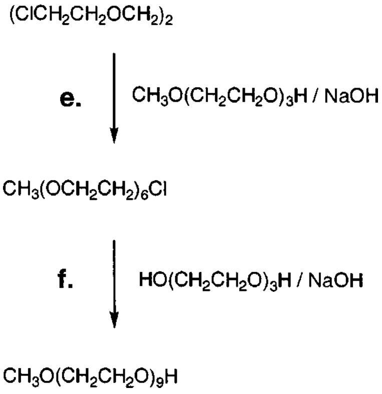


Scheme 2. Reaction sequence yielding the $(EO)_6$ ethoxylate monomethyl ether.

d. The $CH_3O(CH_2CH_2O)_6H$ product (pale yellow liquid, 5.77 g, 0.02 mol, 32%) was purified using Al_2O_3 column chromatography (100% petroleum spirits → EtOAc → 100% EtOH) and preparative RP C_{18} HPLC methods (60 : 40 H_2O : MeOH,8 ml min^{-1}).

Synthesis of HO–(EO)$_9$–Me

The method used for preparation of the HO–$(EO)_9$–Me ethoxylate monomethyl ether is shown in Scheme 3. $CH_3(OCH_2CH_2)_6Cl$ was formed by condensation of $(ClCH_2CH_2OCH_2)_2$ (20 ml, 0.13 mol) and $CH_3O(CH_2CH_2O)_3H$ (20.48 ml, 0.13 mol) under basic conditions (NaOH, 5.17 g, 0.13 mol) with external heating (110 °C, 4.5 h, nitrogen, stirring), step **e.** The $CH_3(OCH_2CH_2)_6Cl$ product was purified by vacuum distillation (b.p. 142 °C, 2 mmHg) at a yield of 17% (3.28 g, 0.01 mol). The $CH_3(OCH_2CH_2)_6Cl$ was then etherified with $HO(CH_2CH_2O)_3H$ (2.2 ml, 0.02 mol) under reflux (19 h, nitrogen, stirring) in THF with NaOH (0.89 g, 0.02 mol), step **f**. An ether–water solvent extraction was performed on the concentrated product mixture and the water-soluble fraction purified by Al_2O_3 column chromatography (100% heptane → EtOAc → EtOH → 100% MeOH) and preparative RP C_{18} HPLC methods (60 : 40 H_2O : MeOH, 8 ml min^{-1}). The $CH_3O(CH_2CH_2O)_9H$ was obtained at 11% yield (0.47 g, 0.001 mol).

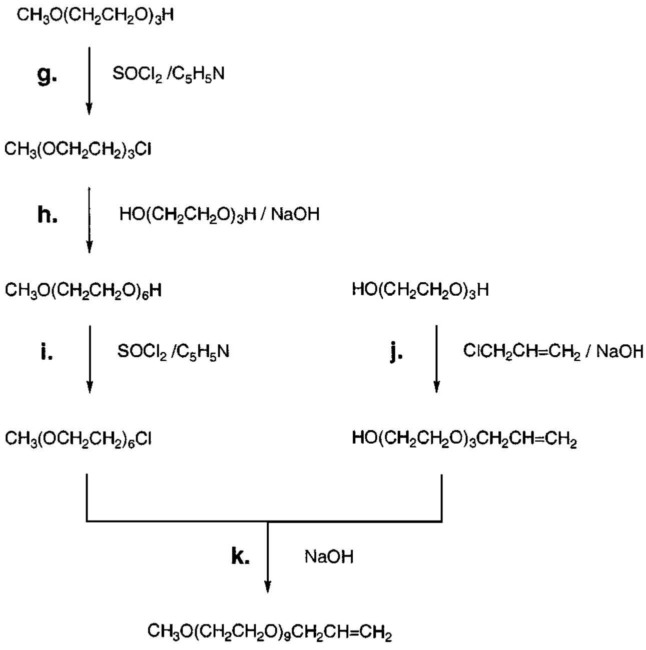


Scheme 3. Reaction sequence yielding the $(EO)_9$ ethoxylate monomethyl ether.

Synthesis of M_2D–C_3–O–$(EO)_9$–Me

A variation on the method for the longer chain oligomer ($n = 9$) was based on the method by Wagner *et al.*,[26] in an attempt to increase the reaction yield. This reaction sequence involved the combination of monochloro triethyleneglycol monoallyl ether with hexaethyleneglycol monomethyl ether (Scheme 4).

The chlorination of $CH_3O(CH_2CH_2O)_3H$ (10.26 g, 0.06 mol) with $SOCl_2$ (23 ml, 0.32 mol) to yield $CH_3(OCH_2CH_2)_3Cl$ was catalysed by pyridine under reflux (5 h, nitrogen, stirring, step **g**). The $CH_3(OCH_2CH_2)_3Cl$ was then added to a heated solution of $HO(CH_2CH_2O)_3H$ (17 ml, 0.12 mol) and NaOH (3.01 g, 0.08 mol) to yield $CH_3O(CH_2CH_2O)_6H$ (5.5 h reflux, 120 °C, step **h**). The unpurified product mixture was then chlorinated with $SOCl_2$ (13 ml, 0.18 mol) under THF reflux in the presence of pyridine (5 h, nitrogen, stirring). The $CH_3(OCH_2CH_2)_6Cl$ product was purified by vacuum distillation (157–160 °C, 2 mmHg) and normal-phase SiO_2 gravity elution chromatography (100% heptane → 100% EtOAc) at a yield of 30% (5.57 g, 0.018 mol, step **i**). $HO(CH_2CH_2O)_3H$ (2.01 g, 0.013 mol) was allylated with $ClCH_2CH{=}CH_2$ (0.75 ml, 0.014 mol) in the presence of NaOH (0.56 g, 0.014 mol) under reflux in THF (25 h, nitrogen, stirring). The product mixture was purified by Al_2O_3 gravity elution chromatography (100% heptane → EtOAc → 100% EtOH) to give $HO(CH_2CH_2O)_3CH_2CH{=}CH_2$ at 69% yield (1.64 g, 0.009 mol, step **j**). The $HO(CH_2CH_2O)_3CH_2CH{=}CH_2$



Scheme 4. Second reaction sequence adopted to yield C_3–O–$(EO)_9$–Me.

was then etherified with $CH_3(OCH_2CH_2)_6Cl$ (step **1**, 2.71 g, 0.009 mol) using NaOH (0.59 g, 0.015 mol) under reflux in THF (24 h). Purified $HO(CH_2CH_2O)_9CH_2CH{=}CH_2$ (2.06 g, 0.004 mol, 51% yield) was obtained by Al_2O_3 chromatography (100% heptane → 100% EtOAc). This was then hydrosilylated (step **b**, 16 h reflux) to give $M_2D{-}C_3{-}O{-}(EO)_9{-}Me$, which was purified by Al_2O_3 column chromatography (0.57 g, 0.0008 mol, 21%) and further by preparative RP C_{18} HPLC (0.24 g, 0.0004 mol, 9% yield).

Spread areas of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions

The oligomer or surfactant product solutions were prepared with 1% w/v Blankophor-P (Ciba Geigy) fluorescent dye and applied as droplets using a micro-syringe (0.24 μl) to the upper surface of recently excised leaves of *Chenopodium album*. The dried droplets were then visualized under UV light using a calibrated JVC TK-1270 colour video camera (Canon FD 50 mm 1 : 3.5 lens) at ×5 magnification. The images were processed with V^{++} Precision Digital Imaging System (IMASCAN) software (Version 4). Multiple droplets (two to six) were applied to each leaf whilst ensuring that droplet overlap did not occur. A minimum of six leaves, all from different plants, was used.

Surface tension of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions

Equilibrium surface tension values of the surfactant solutions (0.2%, 3.2×10^{-3} mol l^{-1}) were obtained by the Wilhelmy plate method, using a Dynamic Contact Angle Analyzer (DCA Series 300, Cahn Instruments Inc.). Values reported are the average of triplicate measurements.

RESULTS AND DISCUSSION

API-MS characterization of L-77

The limitations of existing methods for the analysis of organosilicone compounds have been outlined in the Introduction. In general, nonionic silicone compounds are not readily observed by API-MS methods. However, modified silicone compounds containing groups capable of hydrogen bonding and/or metal-ion complex formation, such as polyethoxylate and amine moieties, can be detected as adducts with H^+, NH_4^+ or alkali metal ions,[27,28] as is observed for polar nonionic molecules.[29] Furthermore, other studies have shown the chelating effect of polyether chains to be unaffected by the introduction of a silicon atom at the beginning of the chain.[30] The application of API-MS–MS to the analysis of volatile methyl-silicon photo-oxidation compounds,[31] of APCI-MS to linear polydimethylsiloxanes and cyclic siloxanes,[32] of ESI-MS to the structural elucidation of the fluorine end-blocked polysiloxanes, $Me_3Si[OSi(CH_2CH_2CF_3)CH_3]_xOSiMe_3$ where $x = 6{-}13$ and to the characterization of reaction products of $Ph_2Si(OH)_2$ with HF,[33] and of ESI-MS for characterizing silatranes[27] and tetraalkoxysilanes[28] have been described.

Nonionic surfactants such as L-77 are detectable by API-MS methods through chelation of NH_4^+, Na^+ and K^+ cations by the polyether chain as shown in Fig. 1. $[M + H]^+$ adducts were not observed even with the use of acidified solvents, including acetic, formic and trifluoroacetic acids. Detection of $M_2D{-}C_3{-}O{-}(EO)_n{-}CH_3$ oligomers was possible in positive ion mode by both APCI-MS and ESI-MS methods, with good response down to absolute injections of 0.1 ng. Ionization in the negative ion mode was negligible at all concentrations analysed, as L-77 has no sites capable of adducting with anions, nor has it any bonds capable of cleavage to yield anionic species.

In the absence of any added salts, the distribution of adducts formed is variable. In general, however, the lower molecular weight surfactant oligomers show a preference for the sodium adduct, whereas the higher oligomers show an increase in preference for the potassium adduct. This is consistent with results from various investigations into the metal-ion complexing abilities of polyether derivatives.[34–40] Only singly charged species of $M_2D{-}C_3{-}O{-}(EO)_n{-}CH_3$ ($n \approx 3{-}16$) were observed for all cone voltages, which is consistent with that expected for the oligomeric distribution of the polyethylene glycol (PEG) constituents.[41,42]

In studies of PEG compounds it was found that more than seven EO units were necessary to bind the K^+ ion in phase transfer experiments,[34] and specific complexations of $(EO)_6$ with Na^+ ions and $(EO)_7$ with K^+ ions were demonstrated.[35] Interactions between $(EO)_8$ and $(EO)_7$ PEGs were observed with the K^+ ion and between $(EO)_7$ and $(EO)_6$ with the Na^+ ion.[36] It was also found that at least five EO units were required for the complexing of PEGs with a K^+ cation-exchange resin.[37] Studies with small-chain PEG compounds ($n = 1{-}4$) showed binding to Na^+ was stronger than to K^+ ions.[38] Similar trends have been observed in the cationization of PEGs with Li^+ versus Rb^+ using MALDI time-of-flight MS.[43]

In general, characteristic fragmentation patterns for this class of compound by API-MS methods have not been observed.[44,45] Increasing the cone voltage did not yield any fragment ions for L-77 by ESI-MS, APCI-MS or FTICR-MS. It has been reported that compared with a proton adduct, structurally significant ions are not generated by collision-induced dissociation (CID) when the parent ion of interest is an alkali-cation adduct.[46] CID fragmentation has been observed for some surfactants by API-MS, but only for protonated species and only for branched alcohol ethoxylates, nonionic surfactants where the polyethoxylate chain is attached to a secondary carbon.[46,47] The conditions used to achieve this CID did not provide fragmentation of the $M_2D{-}C_3{-}O{-}(EO)_n{-}CH_3$ molecules. Internal electron impact (IEI)-FTICR-MS analysis also failed to provide any diagnostic fragment information for these compounds, and this has also been the case for other silicone surfactants under API-MS.[48]

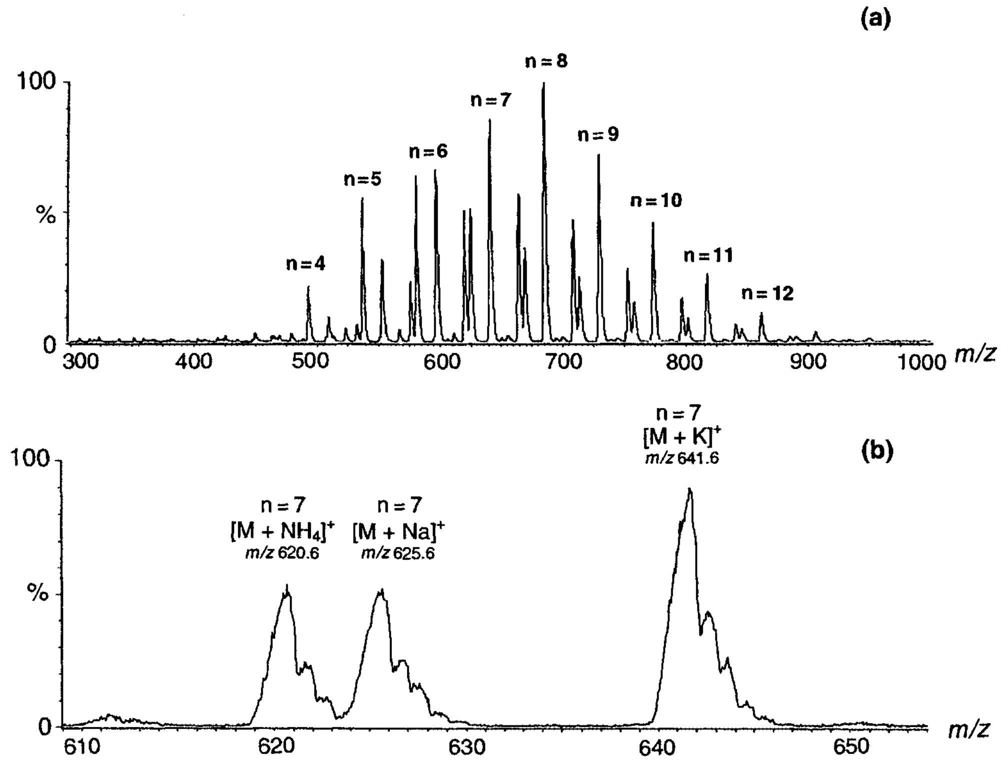
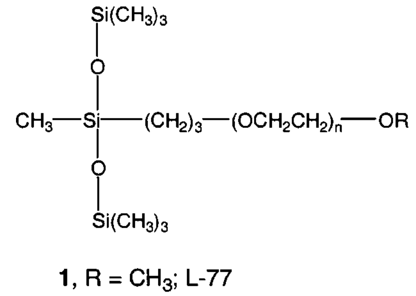


Figure 1. ESI-MS spectrum of L-77: (a) over m/z 300–1000; (b) expanded over the range of the $M_2D-C_3-O-(EO)_7-CH_3$ oligomer.

Identification of by-products in L-77

The reaction employed in the synthesis of the trisiloxane ethoxylate commercial product is always performed with an excess of the alkoxide starting material in order to ensure complete conversion of the Si–H functionality, which may result in an excess of polar constituents. Although removal of these by-products can be relatively easily achieved, it is generally not performed, as comparative investigations have shown no adverse effects on the spreading ability and surface tensions of solutions of L-77, nor on the efficacy of pesticide uptake.[44,49] Quantification of a commercial L-77 blend using RP C_{18} HPLC columns demonstrated that the trisiloxy ethoxylate surfactants $M_2D-C_3-O-(EO)_n-CH_3$ (**1**) and $M_2D-C_3-O-(EO)_n-H$ (**2**) constituted 70% and 5% respectively, with the remaining 25% constituting early eluting polar fractions.[44]


$$CH_3-Si(OSi(CH_3)_3)_2-(CH_2)_3-(OCH_2CH_2)_n-OR$$

1, R = CH_3; L-77
2, R = H; Silwet 408

An HPLC–ESI-MS chromatogram obtained from a commercial formulation of L-77, $(M_2D-C_3-O-(EO)_n-Me)$ is shown in Fig. 2a. Some polar material (early eluting peaks) and the uncapped analogues of the trisiloxy ethoxylate series can also be observed in addition to the $M_2D-C_3-O-(EO)_n-Me$ structures. The $M_2D-C_3-(EO)_n-Me$ oligomers are those peaks eluting between *ca* 35 and 83 min, whereas the $M_2D-C_3-O-(EO)_n-H$ oligomers are observed between *ca* 22 and 35 min. The polar synthetic by-products can be observed eluting early (*ca* 3–10 min) in the chromatogram.

FTICR-MS spectra confirmed the series at 22–35 min to be due to $M_2D-C_3-O-(EO)_n-H$ structures, with the calculated mass and observed mass for the *m/z* 567 peak (sodium ion adduct of the $M_2D-C_3-O-(EO)_6-H$ oligomer) giving identical values (*m/z* 567.2873). All the other oligomers were within 0.0003 amu agreement. This assignment was further confirmed by comparison with the HPLC–ESI-MS chromatograms of L-77 and Silwet® 408 (Fig. 2b). Retention times (22–35 min) and spectra (not shown) were identical for the $M_2D-C_3-O-(EO)_n-H$ oligomers.

Identification and assignment of the other constituents of the commercial mixture was achieved using results from ESI-MS, FTICR-MS, HPLC–ESI-MS and NMR investigations. Consideration of characteristic aspects of siloxane and silanol chemistry, in particular the ability of these compounds to cleave and recondense into a range of linear and cyclic structures, was also necessary in order to elucidate the likely structures (Fig. 3) of the compounds observed. A higher molecular

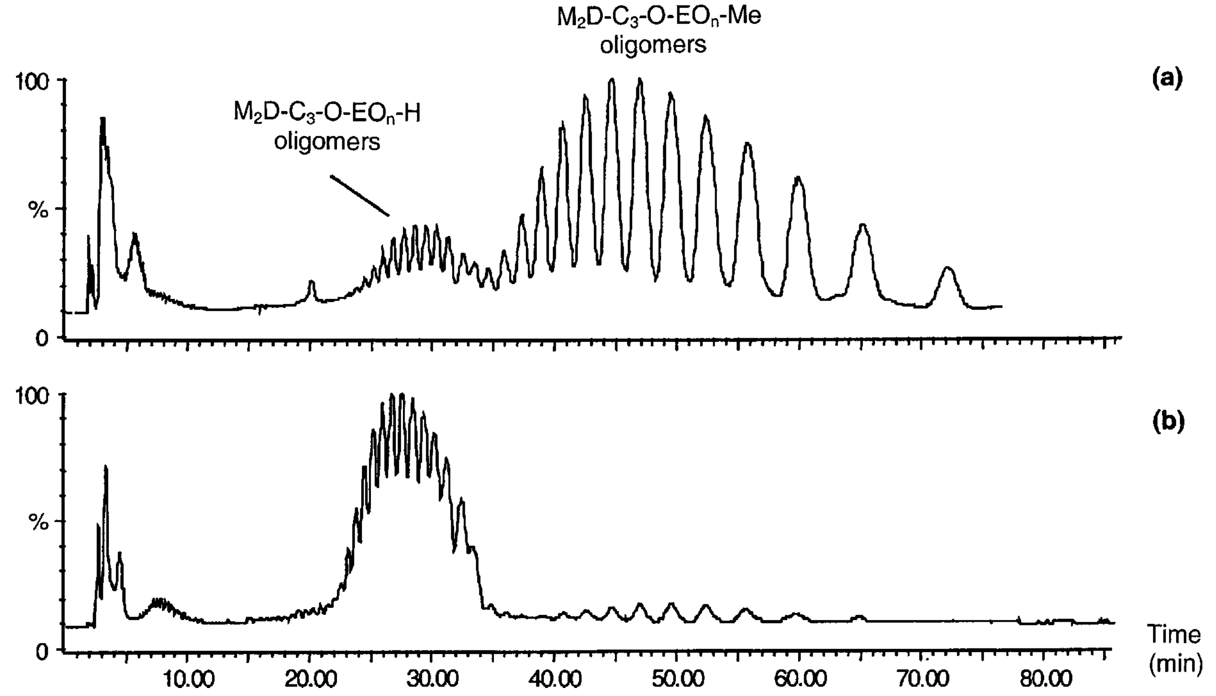


Figure 2. RP C_{18} HPLC–ESI-MS chromatograms of commercial formulations of the trisiloxane surfactants: (a) $M_2D–C_3–O–(EO)_n–Me$ (L-77, 1); (b) $M_2D–C_3–O–(EO)_n–H$ (L-408, **2**).

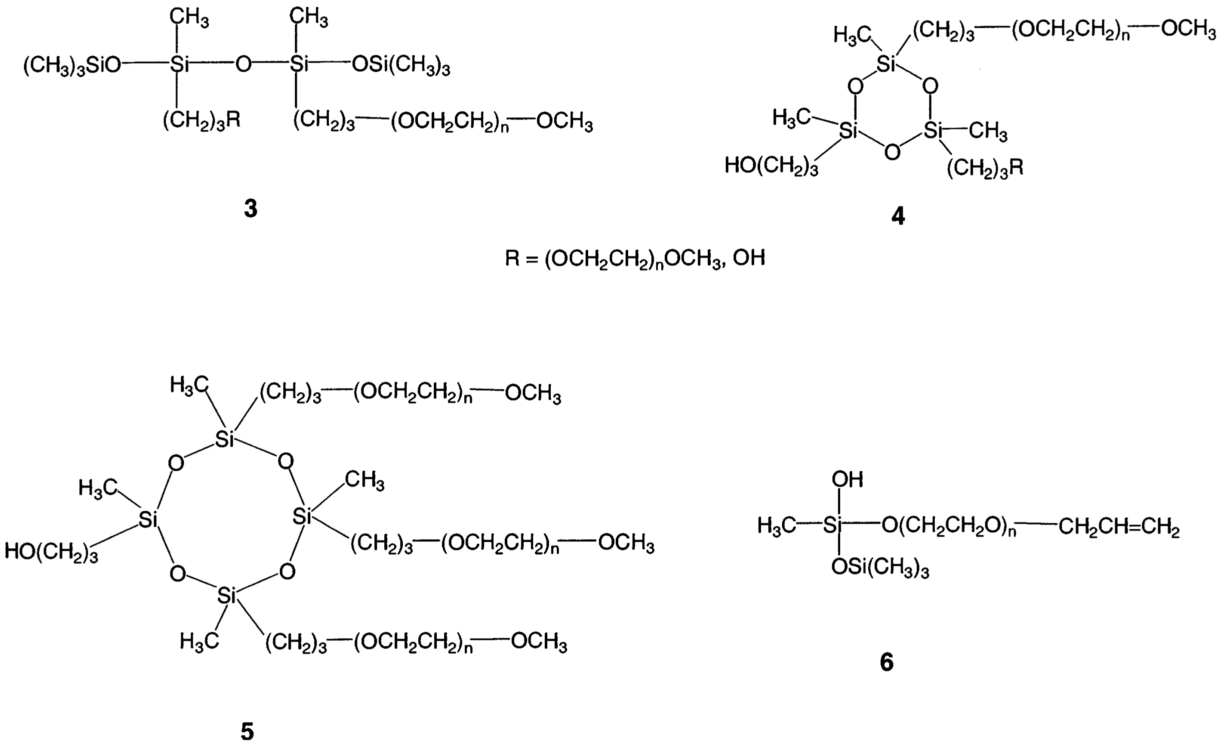


Figure 3. Possible by-products in L-77 as determined by API-MS.

weight series (m/z 934, 978, 1022, 1066, 1109 and 1154) was observed co-eluting with the $M_2D{-}C_3{-}O{-}(EO)_n{-}H$ oligomers, as indicated by the ESI-MS and FTICR-MS spectra. Three plausible structures could be assigned: the linear dimer (**3**, $R = O{-}(EO)_n{-}CH_3$, $n_{TOTAL} = 11{-}16$; $n_{/EOchain\#} = 5.5{-}8$); the cyclic trimer (**4**, $R = O{-}(EO)_n{-}CH_3$, $n_{TOTAL} = 12{-}17$; $n_{/EOchain\#} = 6{-}8.5$); and the cyclic tetramer (**5**, $n_{TOTAL} = 9{-}14$; $n_{/EOchain\#} = 3{-}4.6$).

The linear dimer (**3**, $R = O{-}(EO)_n{-}CH_3$) gives the best agreement between calculated and observed masses and also has the most reasonable ethoxylate chain lengths (Table 1). It is possible that this linear dimer is a synthetic by-product, as it is also a commercially available product (Silwet® 7607).

Analysis of the polar material in the L-77 formulation by ESI-MS also revealed two NH_4^+ adduct series at m/z 400, 444, 488, 532, 576, 620, 664, 708 and m/z 562, 606, 650, 694, 738, 782, 826, 870, 914, 958, 1002, 1046, 1090, 1134. The former series corresponds to oligomers of the by-product **6**. The ions observed correspond to oligomer EO content of $n = 4{-}11$ and the dominant ion for the series (m/z 532) corresponds to the $n = 7$ oligomer of **6**, consistent with the oligomeric distribution of the L-77 product, and thus also the likely distribution of the starting materials.

The formation of **6**, abbreviated to $MD(M^{OH}){-}O{-}(EO)_n{-}CH_2CH{=}CH_2$, can occur through side reactions of the hydrosilylation procedure, resulting in the formation of the Si–O–C linkage.[50] Hydrolysis of a terminal $SiMe_3$ group from the trisiloxyl product would then yield **6**. Comparison of the calculated molecular mass of **6** (m/z 581, $n = 8$) with the high-resolution FTICR-MS data is presented in Table 2. Olefinic resonances (δ_H: 6.2 ppm, d.d; 6.0 ppm, m) were also observed in the ^1H NMR spectrum of the isolated fraction (in D_2O), further supporting this assignment.

The higher molecular weight ion series in the spectrum of the polar constituents corresponds to both the linear dimer **3** ($R = OH$, $n = 3{-}16$) and the cyclic trimer **4** ($R = OH$, $n = 4{-}17$). The Na^+ adducts of this series were also observed by FTICR-MS, comparative calculations of which are shown in Table 2 (m/z 787). The calculated mass for the linear dimer is in better agreement with the observed mass.

Analysis by FTICR–ESI-MS also revealed another $\Delta m/z = 44$ series at m/z 407, 451, 495, 539 and 583, which can be assigned to the free monomethyl polyethoxylates, $CH_3O(EO)_nH$, ($n = 8{-}12$, Na^+ adducts), for which mass difference calculations are well within agreement (Table 2, m/z 407). This was further confirmed by comparison of the HPLC–ESI-MS chromatogram (60 : 40 H_2O/MeOH) with those of commercially available $CH_3O(EO)_nH$ and $CH_3O(EO)_3H$ compounds. Identical retention times and spectra confirmed the $CH_3O(EO)_nH$ assignment. The HPLC–ESI-MS chromatogram also revealed the presence of the uncapped polyethylene glycol ($HO(EO)_nH$) series, which was confirmed by comparison with commercial standards (data not shown).

Spread areas of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions

The average spread areas and dosage calculations for various $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions (0.24 µl droplets) on *Chenopodium album* plant foliage are shown in Table 3.

The 'superspreading' behaviour of L-77 solutions on various synthetic and natural surfaces has been the subject of considerable study.[51] This behaviour has been

Table 1. FTICR-MS characterization of high molecular weight series in the L-77 HPLC fraction eluted over 22–35 min

MW (obs.)	Possible structures[a]	n_{TOTAL}	$n_{/EO\ chain\#}$	Molecular formula	MW (calc.)	$\Delta m/M$ (ppm)
1109.6291	**3**, $R = O{-}(EO)_n{-}CH_3$	15	7.5	$Si_4C_{46}H_{102}O_{20}Na$	1109.5940	32
	4, $R = O{-}(EO)_n{-}CH_3$	16	8	$Si_3C_{46}H_{98}O_{22}Na$	1109.7058	69
	5	13	4.3	$Si_4C_{45}H_{98}O_{21}Na$	1109.5576	64

[a] Refer to Fig. 3 for structures.
[b] Ion series m/z 934, 978, 1022, 1066, 1109, 1154; Na^+ adducts.

Table 2. FTICR-MS data for polar fractions isolated from L-77

MW (obs.)	Possible structures	n_{TOTAL}	$n_{/EO\ chain\#}$	Molecular formula	MW (calc.)	$\Delta m/M$ (ppm)
407.2282[a]	$CH_3O(EO)_nH$	8	8	$C_{17}H_{36}O_9Na$	407.2257	6
581.3475[b]	**4**, $R = O{-}(EO)_n{-}CH_3$	4	2	$Si_3C_{22}H_{50}O_{10}Na$	581.2601	150
	6	8	8	$Si_2C_{23}H_{50}O_{11}Na$	581.2789	118
787.4748[c]	**3**, $R = OH$	8	4	$Si_4C_{31}H_{72}O_{13}Na$	787.3948	102
	4, $R = OH$	9	9	$Si_3C_{31}H_{68}O_{15}Na$	787.3764	125

[a] Ion series m/z 407, 451, 495, 539, 583; Na^+ adducts.
[b] Ion series m/z 449, 493, 537, 581, 625, 669, 713, 757, 801, 845; Na^+ adducts.
[c] Ion series m/z 567, 611, 655, 699, 743, 787, 831, 875, 919, 963, 1007, 1051, 1095, 1139; Na^+ adducts.

Table 3. Spread areas for $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ oligomers[a] on *C. album* foliage

	$n = 3$	$n = 5$	$n = 6$	$n = 7.5^b$	$n = 7.5^c$	$n = 9$	$n = 11$	$n = 13 + 14$
Average spread area per 0.24 μl droplet (mm^2)	1.8	18	50	59	56	50	9	1.7
SD	0.2	3	5	6	7	4	5	0.4
SD(%)	11	14	10	10	13	8	59	22
Dosage (mol mm^{-2})	43	4.3	1.5	1.3	1.4	1.5	8.6	45

[a] 3.2×10^{-3} mol l^{-1} solutions, ambient temperature and relative humidity (~20 °C and 75%).
[b] L-77 (70% $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$, $n = 3$–16).
[c] Purified L-77 (100% $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$, $n = 3$–16).

variously attributed to 'molecular unzippering',[52] or (more scientifically) related to phase behaviour changes,[26,53–56] though in the latter case only the lower oligomers were studied. In agrichemical applications, the behaviour on leaf surfaces is most important. Leaf surfaces can also be characterized as 'easy' or 'difficult' to wet,[57] and *C. album* is in the 'difficult' category. There has been no information on the behaviour of individual L-77 oligomers on leaf surfaces, and from the current data (Table 3) it is clear that there is a huge variation in the droplet spread area. In turn, this causes a more than 30-fold change in actual dose of surfactant per unit area (as nanomoles per square millimetre). In contrast, the presence of up to 25% other materials in the commercial L-77 product does not seem to affect the spreading ability of the mixture. These findings have considerable significance in the use of L-77 as an agrichemical adjuvant.

The average spread area for the $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ oligomers shows a Poisson-type distribution with increasing EO content. Maximum spreading was observed for the L-77 solution (average $n = 7.5$), or the $n = 6$ or 9 oligomers, with very little spreading observed for both the high ($n = 13$ and 14) and low ($n = 3$) oligomers.

These results suggest that the properties of the L-77 mixture are consistent with those of the average oligomer composition $M_2D{-}C_3{-}O{-}(EO)_{7.5}{-}Me$. Other authors have also reported that the spreading behaviour of binary and ternary mixtures of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ oligomers can mimic that of the equivalent single oligomer.[53–56] Also consistent with these results, little spreading was observed for the $(EO)_3$ oligomer solution on the *C. album* plant foliage. Similar spreading trends of $M_2D{-}C_3{-}O{-}(EO)_n{-}H$ solutions on low-energy surfaces have also been described.[58]

Surface tension of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions

The surface tension values observed for the various $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ solutions (Table 4) showed an inverse trend to that obtained for spread area. The lowest surface tension was observed for the L-77 and purified L-77 solutions. The $(EO)_6$ oligomer gave the next lowest value, followed by the $(EO)_9$ solution, with the $(EO)_3$ solution exhibiting a significantly higher value. The L-77 solutions follow the trend of the single oligomer formulations, exhibiting a surface tension value as expected for an oligomer of average $(EO)_n$ content of $n \approx 7.5$.

Table 4. Static surface tension of solutions of $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ with varying EO content

$(EO)_n$	Average surface tension (dynes cm^{-1})	SD	SD (%)
3	27.70	0.11	0.4
6	21.62	0.08	0.4
7.5^a	21.35	0.03	0.1
7.5^b	21.47	0.17	0.8
9	22.73	0.08	0.3

[a] L-77.
[b] Purified L-77.

Low aqueous-solution surface tension is necessary for spreading, and is a notable characteristic of many organosilicone surfactants. The inverse, however, does not apply, as low surface tension does not necessarily equate to efficient spreading. Other surfactants exhibiting lower surface tensions than the organosilicone surfactants show reduced spreading ability.[4] Structural interactions and bulk solution properties of the trisiloxane surfactants are thought to be the cause of the different behaviour, and in particular the compact hydrophobic moiety has been implicated.[59]

CONCLUSION

$M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ oligomers were successfully isolated by RP C_{18} chromatography of L-77. However, this proved to be a highly laborious process, yielding only small amounts of the compounds. Synthetic procedures were investigated and were found to be a more efficient method for obtaining these compounds. Pure $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ oligomers ($n = 3$, 6 and 9) were synthesized by reaction of the corresponding allyl-capped oligoethoxylate monomethyl ether with M_2D^H over a platinum catalyst. The allyl-capped ethoxylate monomethyl ethers were synthesized by reaction of allyl chloride with the corresponding ethoxylate monomethyl ethers ($n = 3$, 6 and 9). The longer chain oligoethylene glycols ($n = 6$ and 9) were prepared by etherification of smaller oligomers.

API-MS has been demonstrated as a valid new technique for the analysis of organosilicone surfactants, whereby valuable new information regarding composition and the characterization of by-products could be obtained. The commercial product L-77 was demonstrated to comprise ∼70% $M_2D{-}C_3{-}O{-}(EO)_n{-}Me$ (**1**), ∼5% $M_2D{-}C_3{-}O{-}(EO)_n{-}H$ (**2**) and ∼25% polar constituents, in addition to a small proportion of the tetrasiloxane linear dimer **3** ($R = O{-}(EO)_n{-}CH_3$). The polar material in the L-77 formulation was found to consist of $MD(M^{OH}){-}O{-}(EO)_n{-}CH_2CH{=}CH_2$ (**6**), the tetrasiloxane linear dimer (**3**, R = OH), the free monomethyl polyethoxylates ($CH_3O(EO)_nH$), and uncapped polyethylene glycol ($HO(EO)_nH$).

Although the spreading behaviour of L-77 and its oligomers has previously been studied in some detail, this has been on artificial surfaces. The present results confirm that similar spreading trends occur on equivalent plant leaf surfaces.

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