

Analysis of nonionic surfactants and silicone polymers in cosmetic products using Matrix - assisted Laser Desorption/ Ionization Time-of- flight Mass Spectrometry

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Summary

A rapid and efficient method for analyzing the nonionic surfactants and silicone polymers, which control the shape and characteristics of cosmetic products and give influence on product quality, has been developed using Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI- TOF /MS).

The MALDI-TOF/MS could easily and effectively determine the molecular weight distribution and monomer units of nonionic surfactants. As a result, creating a library of mass spectrum data of surfactants used in cosmetic products using MALDI-TOF/MS and analyzing surfactants extracted from the products may become a useful method for detailed structural characterization of the surfactants.

Furthermore, the MALDI-TOF/MS analysis was effective in obtaining the spectrum of silicone polymers from which the molecular weight distribution could be determined. The repetition units and structural data could also be obtained through molecular mass peaks. Additionally, the monomer ratio and terminal groups as properties of silicone copolymers could be determined

Introduction

A variety of macromolecular species including silicon macromolecules and surfactants are used in cosmetic products to stabilize their consistency and to improve their feel. Analysis is often difficult since these compounds are large in size and usually nonvolatile. However, since these compounds have a large impact on the quality of the product, a method for determining the molecular weight and molecular weight distribution of polymers is necessary.

Non-ion surfactants are extensively used in cosmetic, medical, domestic and industrial products for the purpose of detergency, emulsification, wetting, and foaming. Non-ion surfactants are classified into ether, ester, and amide forms according to their structure. It may also be classified into polyoxy ethylene (POE) added form and non-POE form. Of these, the non-POE form is often used in cosmetic products but their analysis is often extremely difficult due to their large molecular weight and their distribution as a mixed compound. Recently, the usage of silicone copolymer with added ethylene oxide is increasing and their methods of analysis are being developed in a number of different ways.

The known methods of analyzing non-ionic surfactants are IR, TLC¹, wet chemical techniques and NMR. Even though these methods yield the chemical property of the surfactants, they cannot be used to determine molecular weight distribution, the extent of EO addition in POE, monomer ratio of copolymers and identification of terminal groups. Even though simple non-ionic surfactant composition may be determined through TLC¹, elementary analysis², HPLC^{3,4}, SFC^{5,6} or NMR⁶, these methods are limited when the sample composition is complex or if the molecular weight is large. Also methods using GC^{7,8} or GC-MSD can be used either directly or through TMS, but is limited to around 16~18 moles of EO additives. The method is ineffective if the added mole number is larger than the limit or if the compound is nonvolatile.

On the other hand, the mass spectrum obtained from Matrix - assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/MS) determines the molecular weight and

molecular mass distribution more rapidly and accurately. MALDI-TOF MS is a recently introduced^{9,10} soft ionization technique that allows desorption and ionization of very large molecules, even if in complex mixtures. In polymer analysis,¹¹⁻²³ the great promise of MALDI-TOF is to perform the direct identification of mass-resolved polymer chains including intact oligomers leading to measurement of molecular weight (MW) averages and molecular-weight mass distribution (MWD) and the simultaneous determination of the structure and terminal groups. All the conventional MW characterization techniques (viscosity, GPC, laser light scattering) are indirect measurements of molecular masses and the perspective of direct measurements of MW and MWD has stirred much expectation among polymer scientists, but the characterization of synthetic polymers by MALDI-MS is far from satisfactory.²⁴ In fact, it has been found²³ that molecular weight estimates provided by MALDI-MS agree with the values obtained by conventional techniques only in the case of samples with a narrow MWD,²³ whereas with polydisperse polymers MALDI-MS fails to yield reliable MW values. In case of copolymers, the determination of monomer ratio and terminal groups is also possible.²⁵

In this study, a method of analyzing the molecular weight distribution and the extent of EO addition of POE added surfactants and silicone polymers widely used in cosmetic products was developed using MALDI -TOF Mass.

Materials and methods

Materials

2,5-Dihydroxybenzoic acid (DHB), 2-(4-hydroxyphenylazo) benzoic acid (HABA), silica gell (70-230 mesh) and Na₂SO₄ anhydride were purchased from Sigma (St. Louis, MO, USA).

Methanol, chloroform, ethylacetate, acetone were obtained from Burdick & Jackson (MI, USA).

Tween 20 (polysorbate 20), Tween 60 (polysorbate 60) were purchased from Aldrich. Myrj 52 (PEG 40–stearate), Myrj 59 (PEG 100–stearate), Brij 35 (Laureth-23) and Brij 721 (Steareth-21) were purchased from Uniqema America.

Silicone polymers and copolymers modified with ethylene oxide were obtained from Dow Corning Corporation, Shin Etsu Silicones of America, Inc. and Goldschmidt Chemical Corporation.

MALDI sample preparation

HABA and DHB were used as matrixes. All the samples were dissolved in chloroform at a concentration of 0.5% (wt/vol). HABA was dissolved in the mixed solvent (water:acetonitrile = 1:1) at a saturation. DHA was dissolved in acetone at saturation. 1ul of the matrix solution and 1ul of the sample solution were pipetted onto a stainless steel sample slide and air-dried.

MALDI-TOF mass spectra

All mass spectra were obtained on a modified Voyager-DE STR MALDI-TOF mass spectrometer (PerSeptive Biosystems, Framingham, MA, USA) reflector mode. The MS spectra were obtained in delayed extraction mode using an accelerating voltage of 20 kV and 150 ns delay. Desorption and ionization of sample occurred with a nitrogen laser ($\lambda = 337$ nm). The original data acquisition system was replaced by a Tektronix TDS 540C 2 GS/s digital storage oscilloscope (Tektronix Inc., Beaverton, USA).

Isolation of non ionic surfactants from commercial cosmetic products

Preliminary treatment of product 1

1-3g of sample was measured, dissolved in chloroform and filtered. The filtrate was applied to a column that has been packed with 20g of silica gel (70-230 mesh) and 10g of anhydrous sodium sulfate. The column was eluted with the following solvents (50ml per fraction). Fraction containing the POE added surfactant was determined by the Dragendorff's reagent and dried by vaporization. The NMR, IR and MALDI-TOF/MS analyses of the remnants were conducted, their weights were determined and the POE added surfactants quantified.

1. Chloroform 200ml
2. Ethylacetate/Chloroform Mixture (1:99) 100ml
3. Ethylacetate/Chloroform Mixture (1:1) 100ml
4. Acetone/Chloroform Mixture (1:1) 100ml
5. Methanol/Chloroform Mixture (5:95) 100ml
6. Methanol/Chloroform Mixture (1:9) 100ml

7. Metanol/Chloroform Mixture (1:2) 100ml

Preliminary treatment of product 2

As the result of remainder after drying, ash, NMR and GC analysis, 1,3-buthylene glycole (BG), Zeolite, PEG (polyethylene glycol) and a small amount of Silicone was detected. In order to selectively extract PEG, the sample was thoroughly dried at 105°C to remove 1,3-BG. Ethanol was added to the remnants and filtered to remove zeolites and PEG was selectively obtained by vaporization.

Results and discussion

Analysis of non-ionic surfactants used as ingredients in cosmetic products

Matrix has a large effect on the ionization of samples. Therefore, it is crucial to find an appropriate matrix that is suitable to the sample. Organic acids such as ferulic acid, DHB^{26,27}, HABA and CHCA²⁸ (α -cyano-4-hydroxycinnamic acid) are generally used in MALDI analysis since they absorb ultraviolet light well and can act as proton donors. DHB and HABA are usually used when determining the molecular weight of non-polar or slightly polar compounds and macromolecule compounds. CHCA is usually used for biological samples such as proteins or peptides. Ferulic acid is widely applicable in a variety of compounds and can determine a wide range of molecular weights. The reason that the matrix is predetermined according to the samples is due to the differences in proton affinity of the two. In order to determine the suitable matrix for the surfactant, both DHBA and HABA were applied and found out that both were able to form ions for the spectrum.

The advantage of weight determination methods for macromolecule compounds with small molecular weight is that compared to existing methods such as gel permeation chromatography/size exclusion chromatography (GPC/SEC) and light scattering, is that not only are they rapid and accurate but can determine repeat units and their molecular weights as well.²⁵ Figure 1 depicts the structure of non-ionic surfactant used in cosmetic products. The mass spectrum of such non-ion surfactants was obtained by using HABA and DHB as the matrix and by obtaining crystals through natural drying. The mass spectrum of Figure 2 is that of PEG 300. The peaks of the ions $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$ is visible and it can be seen that the $[M + Na]^+$ ion shows the largest peak. The molecular weight distribution and repeat units may be determined by calculating the differences in molecular weight peaks.

The molecular ions of mass spectrum (a) and (b) in Figure 3 were confirmed through the

spectrums of Tween 20 (polysorbate 20), Tween 60 (polysorbate 60). Their molecular distribution and repetition units (44 u) were determined. The representative structure of the Tween groups was confirmed as the macromolecule compound consisting of the sorbitol ester compound shown in Figure 1 and an anhydride compound. In other words, the molecular weight distribution consisted of more than two peaks. Since their distribution was different, it is possible to differentiate between the same groups.

The molecular ions of mass spectrum (a) and (b) in Figure 4 were confirmed and their molecular distribution and repetition units were determined through the spectrums of Myrj 52 (PEG 40 – stearate) and Myrj 59 (PEG 100 – stearate). Differentiation between the same groups as well as other surfactants was possible.

The (a) and (b) in Figure 5 are the mass spectrum of Brij 35 (Laureth-23) and Brij 721 (Steareth-21). The Brij 35 compound is an ether of lauryl alcohol with ethyleneglycol as the adding group and Brij 721 is an ether of stearyl alcohol with ethyleneglycol as the adding group. The structure of the latter is depicted in Figure 1. The molecular weight, the distribution and the repetition rate were determined. These results for the non-ionic POE surfactants are briefly summarized in Table I.

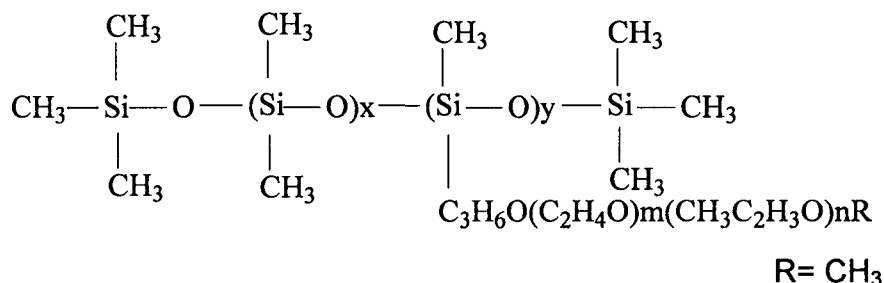
Analysis of silicon polymers used as ingredients in cosmetic products

In order to determine the suitable matrix for silicon macromolecules, DHB, dithranol and HABA were applied. As a result, molecular ion spectra of dimethicone A (Dow Corning 200 Fluid (Figure 6 (a)) and dimethicone B (Kf 96a 30CS (Figure 6 (b)) were obtained using DHB and HABA. According to these spectrum, the molecular weight range in dimethicone A is distributed between $m/z = 1000 - 3000$ and the difference between peaks is $73 - 75 \text{ u}$ ²⁵. The difference of $73 - 75 \text{ u}$ is within the difference in dimethylsiloxane (DMS) units. The molecular weight range in dimethicone B spectrum was distributed between $m/z = 1000 - 4500$ and the peak difference was also $73 - 75 \text{ u}$.

Also, using DHB as the matrix, molecular ion spectra of Dimethicone 6CS (Figure 7 (a)), 20CS (b), 30CS (c) and 50CS (d) were obtained. The molecular weight distribution of Dimethicone 6CS spectrum was between $m/z 1200 - 1800$. The difference between the peaks was $73 - 75 \text{ u}$, which is an evidence of DMS repeat unit and the distribution of silicon macromolecule compound. The Dimethicone 20CS spectrum also shows a mass difference of $73 - 75 \text{ u}$ between the peaks in the molecular weight range of $100-3000$. The difference between the spectrums of Dimethicone 30CS and Dimethicone 20CS were small. Therefore, the difference between 20CS and 30CS can be confirmed by GC analysis. However, the Dimethicone 50CS spectrum shows a larger molecular weight range than either the 20 or 30. The molecular weight range was between $1000-4000$ and the mass difference between the peaks was $73 - 75 \text{ u}$, which confirms the repetition unit as DMS.

PEG-12 Dimethicone (Dow Corning 193 surfactat) is the polyethylene glycol derivative of Dimethicone (q.v.) containing an average of 12 moles of ethylene oxide and used as a surfactant. Bis-PEG-18 Methyl Ether Dimethyl Silane (Dow Corning 2501 cosmetic wax) is a dimethyl silane ethoxylated methyl diether containing an average of 36 moles of ethylene oxide. The mass spectrum of these macromolecules were obtained by using HABA and DHB as the matrix. The common mass peak of PEG-12 Dimethicone and Bis-PEG-18 Methyl Ether Dimethyl Silane spectrum can be seen in Figure 8. The weight distribution of PEG-12 Dimethicone (Figure 8(a)) in

the range of $m/z = 350 - 1000$. By calculating their molecular weight in the manner shown below, it is possible to check the peak series shown in Table II.



M/z of sodium ion in POE added silicon macromolecule = $89.190 + 74.155x + (117.200 + 44.053m + 58.080n)y + 15.035 + 22.990$

The spectra of Bis-PEG-18 Methyl Ether Dimethyl Silane shows a molecular weight distribution in the range of $m/z 400 - 1450$ and the molecular weight peak consists of series in $x=0, y=1, m=1, 2, 3, 4, 5 - 28, n=1$.

Determination of surfactants used in cosmetic products

In order to determine surfactants in cosmetic products, basic chemical tests are conducted and then each component separated by column chromatography and quantified. Next, spectral analysis such as NMR or IR is conducted to determine surfactants (Qualitative analysis).

The result of NMR spectrum analysis of the surfactant extracted from product 1 shows a triplet (CH_3 peak) peak at 0.8ppm, multiplet (CH_2 peak) peak at 1.2ppm and a broad singlet (POE peak) at 3.6ppm, which points to an alkyl ether type of surfactant. As can be seen in Figure 9, the molecular weight distribution is in the range of 500-2800 and the added POE mole number was determined to be around 10-40 moles.

It was found that the same surfactant may have different molecular weight distribution and different physical properties depending on the manufacturer. The surfactant, steareth-21 (Figure 10

(a) produced by company A and steareth-21 (Figure 10 (b)) produced by company B were used in the hair colorant (Table III) and was shown that the two displayed differing physical properties. This was due to the difference in the molecular weight distribution of the surfactants produced by the two companies.

The surfactant extracted from product 2 was determined to be a PEG group from the NMR analysis result, which showed a broad singlet at 3.6ppm. However, the molecular distribution was difficult to determine. The molecular distribution was determined from Figure 11 and was found identical to that of PEG 400.

Conclusion

It was found that MALDI-TOF/MS could easily and effectively determine the molecular weight distribution and repetition units of surfactants. Therefore, creating a library of mass spectrum data of surfactants used in cosmetic products using MALDI-TOF/MS and analyzing surfactants extracted from products may become a useful method for determining the properties of surfactants.

Also, MALDI-TOF/MS analysis was effective in obtaining the spectrum of silicon macromolecules from which the molecular weight distribution could be determined. The repetition units and structural data could also be determined through the molecular mass peaks. The monomer ratio and terminal groups may also be determined in the case of silicone copolymers. This method may be useful in the determination of properties of silicon macromolecules extracted from products in a rapid and accurate manner.

MALDI – TOF/MS method could be a useful and simple method in qualitative analysis of polymer and surfactants included in cosmetic materials and special shapes of products other than materials presented in this paper.

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Table I. Distributions of the molecular weight, Repeat unit, and Numbers of ethylene oxide of non-ionic surfactants

Surfactants	Distributions of the molecular weight	Repeat unit	Numbers of ethylene oxide (n)
1. PEG 400	300 – 800 monodispersion	44	5 - 15
2. Tween 20	300 – 800 : 900 – 2000 polydispersion	44	3 - 30
3. Tween 60	400 – 800 : 900 – 2500 polydispersion	44	5 - 35
4. Tween 80	500 – 1100:1200 – 2500 polydispersion	44	8 - 35
5. Myrij 52	1200 – 3000 monodispersion	44	20 - 60
6. Myrij 59	500 – 5000 polydispersion	44	10 - 100
7. Brij 35	600 – 2000 monodispersion	44	10 - 40
8. Brij 721	600 – 2000 monodispersion	44	10 - 100

Table II. Sodiated molecular ion data-base with structural information (x: number of DMS units; y: number of MPOS unit; m: number of ethylene oxide; n: number of propylene oxide)

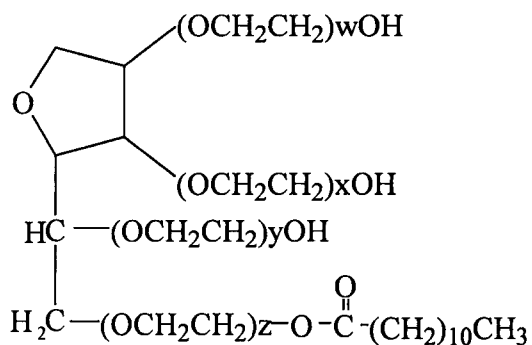
x	y	m	n	M + Na
1	1	0	0	319
0	1	2	0	333
0	1	1	1	347
1	1	1	0	363
0	1	3	0	377
0	1	2	1	391
1	1	2	0	407
0	1	4	0	421
0	1	3	1	435
1	1	3	0	451
0	1	5	0	465
0	1	4	1	479
1	1	4	0	495
0	1	6	0	509
0	1	5	1	523
1	1	5	0	539
0	1	7	0	553
0	1	6	1	567
1	1	6	0	583
0	1	8	0	597
0	1	7	1	611
1	1	7	0	627
0	1	9	0	641
0	1	8	1	655

Table III. Preparation of hair colorant

Raw materials	% of Weight
Dehydag Wax	7.5
Steareth-21	3.0
Laureth-9	2.5
GMS 105	2.5
EDTA-2Na	0.2
STAC	0.5
Glycerine	1.5
Ammonia	q. s.
Perfume, preservative, color	q. s.

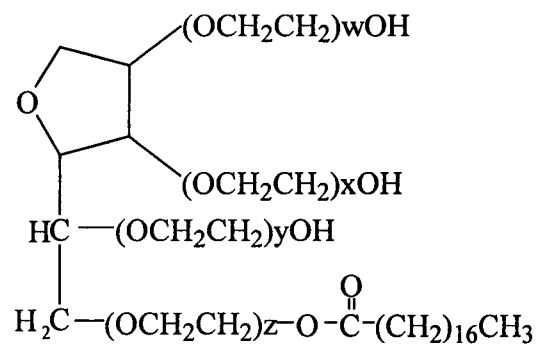
$H(OCH_2CH_2)_nOH$

PEG 400 (polyethylene glycol 400 n = 400)



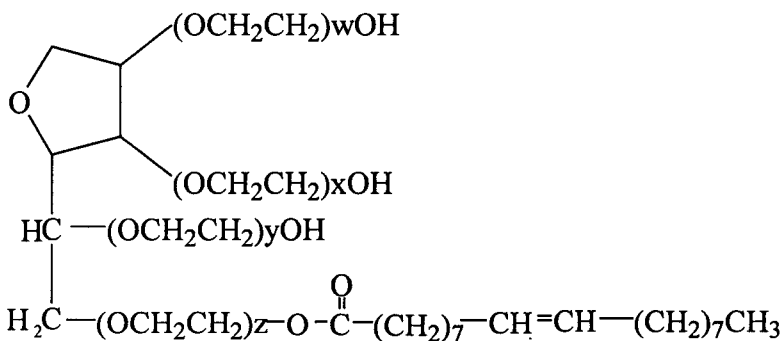
Tween 20 (polysorbate 20)

$$w + x + y + z = 20$$



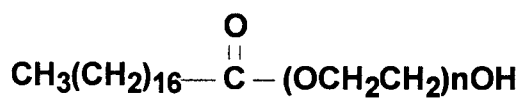
Tween 60 (polysorbate 60)

$$w + x + y + z = 20$$



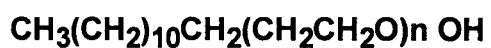
Tween 80 (polysorbate 80)

$$w + x + y + z = 20$$



Myrij 52(PEG-40-stearate n = 40),

Myrij 59 (PEG-100-stearate n = 100)



Brij 35 (Laureth-23 n = 23)



Brij 721 (Steareth-21 n =21)

Figure 1. Structure of non ionic surfactants in cosmetic raw materials