Secondary Ion Mass Spectrometry of Monomolecular Layers of Fatty Acids Prepared by Langmuir-Blodgett Techniques

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Abstract: A novel approach to the examination of static secondary ion mass spectrometry (SIMS) sampling and ionization mechanisms is demonstrated by utilizing Langmuir-Blodgett techniques for producing monomolecular layers. This method offers advantages over those reported previously in that a model system can be engineered and the physical state and orientation of large molecules on a polycrystalline metal surface can be precisely controlled. A series of five (saturated and unsaturated) fatty acid monolayers was prepared on cleaned silver surfaces, and positive and negative static SIMS results are reported from argon ion bombardment. Results showed that molecular and quasi-molecular ions are produced and can be detected from a single monolayer. The degree of cationization by silver from the substrate is dependent on the extent of surface oxidation and is only observed for unsaturated fatty acids. The degree of unsaturation was also readily detected from both fragmentation and molecular ion production. Analysis of LB multilayers of stearic acid on silver shows that even with an ordered deposition of 375 Å, the silver ion signal is not totally diminished, due to the high vapor pressures of the substrate. These results taken together support a cationization process of attachment in the selvage vapor phase for the oriented molecules.

The use of secondary ion mass spectrometry (SIMS) as a means of elucidating surface molecular structure has recently gained importance following the development of "static" or low-damage experimental conditions.[1,2] Mechanisms of ion formation in the SIMS analysis of large molecules are not entirely understood. One reason for this is the lack of well-characterized model systems and subsequent control over sample production. Detailed studies of ion formation and ejection have been recently accomplished for submonolayer adsorption of small molecules on metal surfaces by Winograd et al.,[3,4] demonstrating the sensitivity of angle-resolved SIMS to different molecular orientations which occur under various coverages. Colton and Campana[5,6] have studied the ejection of large inorganic "cluster" ions from pure inorganic compounds, also showing the dependence of preexisting structure on ion emission probability. The present research demonstrates that a viable model system for examining the SIMS sampling process for large organic molecules can be developed with the use of Langmuir-Blodgett (LB) techniques[7,8] to produce a highly oriented monomolecular layer prepared on a well-characterized solid substrate. The use of LB methods to engineer well-characterized systems offers the following novel advantages for SIMS: (i) a highly regular and pure model system can be prepared, (ii) molecular orientations for large molecules are precisely determined, (iii) modifications such as substrate changes, added cations, and chromophores can be effected, and most importantly the "physical state" of the monolayer can be changed by varying the applied surface tension during production.[9] In addition, ancillary techniques such as ellipsometry, infrared spectroscopy, and thermodynamic measurements (force area (FA) isotherms) can corroborate the nature of the monolayer.[9] Allied with LB techniques, the present results show that SIMS possesses the requisite sensitivity to probe monolayers on a molecular scale, observing molecular and quasi-molecular ions produced from the model systems and differentiating between saturated and unsaturated fatty acids.

Previous SIMS studies of systems prepared with LB methods have focused only on multilayers of fatty acid salts.[10,11] Laxhuber and Mohwald studied cadmium arachidate multilayers and reported "destruction" rates for SIMS using dynamic conditions.[10] Toyokawa et al. produced cobalt stearate multilayers with LB methods and monitored the Co^+ signal as a function of the number of layers.[11] In these previous studies of LB systems, dynamic SIMS conditions were employed, and indeed, surface destruction resulted in a lack of observed molecular and quasi-molecular ions related to the fatty acid structure or the substrate. These conditions would quickly destroy the integrity of the multilayer

systems but were used to increase the sensitivity of the technique. Colton et al. studied fatty acids prepared from melt on cleaned chromium surfaces by SIMS.[12] They noted the detection of very few structurally related ions, and these were monitored over long sputter times as a function of fatty acid chain length. Colton et al. noted that the detection of molecular ions may have been hampered by their secondary ion filtering conditions.[12]

We have employed static conditions throughout our work on organic systems,[13-15] stressing that the limitations on primary ion beam current density, energy, and total ion dose reduce sample disruption, decrease fragmentation, and thus benefit the production of structure related molecular and quasi-molecular ions.

The results presented in this work constitute the first report of static SIMS analysis of fatty acids where molecular and quasi-molecular ions are observed. In addition, the detection of these ions from a single (quantified) monomolecular layer demonstrate the promise of the LB technique for producing a homogeneous model system of large molecules in which orientation may be controlled, opening a way of exploring the sensitivity of static SIMS to the relationship between molecular species and substrate, the "preionized state",[1] and the final emitted molecular ion.

Experimental Section

For this work, a series of saturated and unsaturated fatty acids (listed in Table I) (Sigma Chemical Co., chromatographic reference grade, >99% purity) was used to prepare the monolayers without further purification. The acids used varied in chain length from 12 to 18 carbons

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Monomolecular Layers of Fatty Acids

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Table I. Results of SIMS Analysis of Fatty Acids (+ Indicates Presence Observed, − Absent)

triv name	lauric	palmitic	stearic	oleic	linolenic
IUPAC name	dodencanoic acid	hexadecanoic acid	octadecanoic acid	9,2,15-octadecatrienoic acid	*cis*-9-octadecenoic acid
M_r	200.33	256.42	284.47	282.45	278.42
no. of C's	12	16	18	18	18
form	$CH_3(CH_2)_{10}COOH$	$CH_3(CH_2)_{14}COOH$	$CH_3(CH_2)_{16}COOH$	$CH_3(CH_2)_7CH=CH-(CH_2)_7CO_2H$	$CH_3(CH_2CH=CH)_3CH_2-(CH_2)_6CO_2H$
approx thickness of monolayer,[12] Å	17.1	22.2	24.7	24.7	24.7
posit ions					
M^+	−	−	−	−	−
$(M + H)^+$	−	+	−	−	−
$(M + Ag)^+$	−	−	−	+	+
$(M + Na)^+$	+	−	+	−	−
$(M + Na - CO_2)^+$	−	+	−	−	+
$(M + Na - CO_2H)^+$	+	+	+	+	−
$(M + Na - HAc)^+$	+	+	−	+	+
$(M + H - HAc)^+$	+	−	−	−	+
$(M + H - CO_2H)^+$	−	+	−	−	+
$(M + H - CO_2)^+$	+	+	−	−	−
negat ions					
M^-	+	+	+	+	+
$(M - H)^-$	+	+	+	+	+
$(M + Cl)^-$	−	+	−	+	−

(i.e., 17–25 Å) and in degree of saturation in the C_{18} acids. High-purity polycrystalline silver foil (Alfa, 99.999%), 0.25 mm thick, was employed as a substrate. Coupons of Ag were washed with detergent, rinsed with tap water, and then copious amounts of triply distilled (in quartz) water. These cleaned substrates were then plasma-oxidized at <50-W rf power in air at 0.1 torr for 6 min. This technique has been shown to provide a high-energy (>60 dyn/cm) surface free of detectable organic constituents,[16] with a thin oxide coating.

The LB trough employed has been described in detail previously.[17] Briefly, it is constructed completely of Teflon, with a Wilhelmy plate magnetic transducer assembly for surface tension measurements. Solutions (0.1 mg/mL) of the fatty acid in benzene (ACS Reagent Grade) were delivered with a microsyringe to the trough substrate which was triply distilled (in quartz) water. After equilibration at a specified surface tension which corresponded to a condensed (solid) state, the substrates were lifted slowly while constant surface tension was applied through a servomotor feedback system. All sample preparation was accomplished in a class 1000 cleanroom.

The SIMS instrument used was a Leybold Heraeus LHS10 modified for organic SIMS and will be described in detail elsewhere.[18] The unit utilizes argon gas in a cold cathode ion source and a Balzers quadrupole mass filter (1–1000 amu). The ion gun was differentially pumped and operated at a pressure of 8×10^{-9} mbar with a system base pressure of 8×10^{-11} mbar. Sample bias voltages of ± 22 V were applied to an insulated sampling rod to increase measured ion yield.[18] The ion current densities ranged from 1 to 5 nA/cm² (referenced to a Faraday cup) from the beam which was defocused and rastered over a 4 × 4 mm area. A flood gun was available but not used.

Results and Discussion

Table I indicates the results of both positive and negative ion spectra of the various fatty acids used in the investigation. The assignments made are based upon classical mass spectroscopic fragmentation patters[19] and also from similar work by ^{252}Cf mass spectrometry by Zoeller[20] of behenic acid. Table I illustrates that M^+ and $(M + H)^+$ are not generally observed in the positive ion spectra. The exception is where $(M + H)^+$ was seen as a weak feature in the spectrum of palmitic acid. These observations are readily explained by the impossibility of assigning a stable and chemically sensible resonance structure to either a positive molecular or protonated fatty acid species. Protonation via intermolecular hydrogen transfer at the acid head functionality is precluded in this case because of the absence of dimerization in the monolayer which would occur in an unorganized or a multilayer system.

The presence of signals from the $(M + Ag)^+$ silver cationized molecule was only observed from unsaturated fatty acids in the monolayer. While these features are weak, the lack of $(M + Ag)^+$ signal from saturated fatty acid monolayers yields some important mechanistic conclusions. Firstly, analysis of fatty acids prepared from solution onto chemically oxidized silver surfaces yields strong signals from protonated and sodium and silver cationized molecules.[21] Extrapolation of signal intensities from these experiments to the effective concentration of the LB monolayer system would suggest that detection of cationization is suppressed by the specific preexisting orientation of the molecule on the sample surface in the LB monolayer. Differences in surface area and oxide layer thickness between wet oxidation and plasma glow discharge oxidation could also account for this suppression. Secondly, it appears that the mechanism of attachment involves silver ion complexation to the double bond along the chain which must occur during the bombardment process. Thus, the lack of cationized signal when the fatty acid head is oriented at the silver surface indicates that the cationized molecule is not ejected as a preexisting structure.

Preliminary experiments[21] also show that multilayers of 15 stearic acid molecules (375 Å) deposited in a "Y" configuration[9] do not block Ag^+ emission but do attenuate signal from the Ag cluster ions. The volatility of silver would support the idea of a high concentration of Ag^+ ions available for the attachment. Signals from quasi-molecular ions are also diminished from the multilayers, but further investigations are in progress. Sodium cationization was observed only in the spectra of palmitic, oleic, and linolenic acids and at a low intensity. This confirms the result of the quite careful steps taken to exclude Na contamination (c.f. Figures 1A and 2A) during the monolayer production process. Quasi-molecular ions from neutral losses from Na-cationized molecules are observed however (such as $(M + Na - CO_2)^+$, $(M + Na - CO_2)$,$^+$ $(M + Na - CO_2H)^+$, $(M + Na - HOAc)^+$) at fairly high intensities, which leads us to conjecture that the Na-cationized neutral loss ions are stable compared to the $(M + Na)^+$ emissions. In addition, loss features from the protonated fatty acid parent ions were seen (i.e., $(M + H - HAc)^+$, $(M + H - CO_2H)^+$, $(M + H - CO_2)^+$) with the decarboxylation being quite pronounced. This is regularly observed in the classical mass spectroscopy of organic acids.[19]

As one would expect, fatty acids readily form anions and anionic radicals due to the stability inherent in delocalizing charge over

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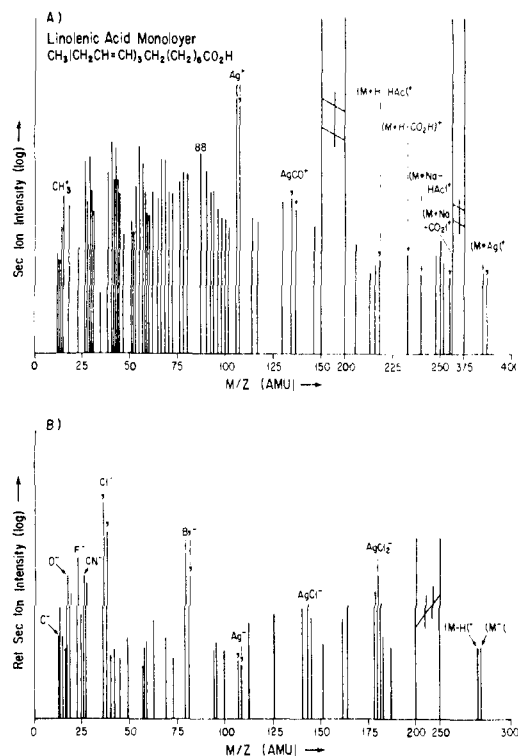(21) Wandass, J. H.; Gardella, J. A., Jr., unpublished results.
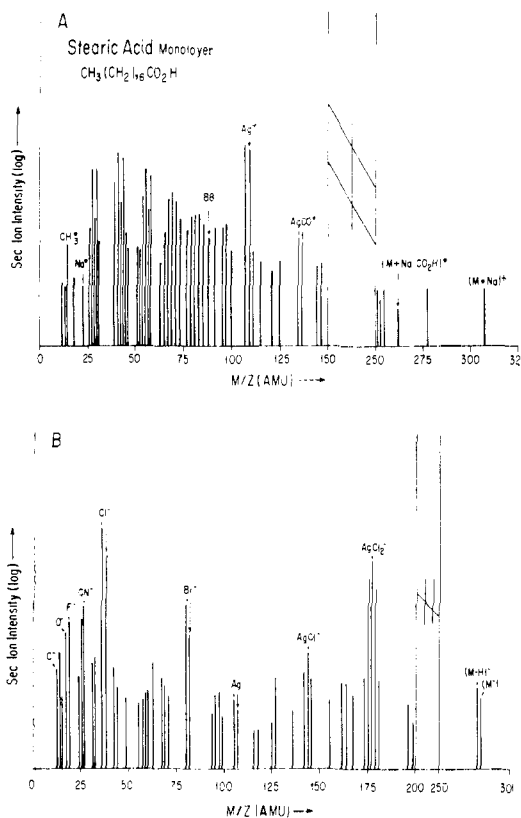
Figure 1. Static SIMS spectra of single monolayer of stearic acid prepared and transferred to a cleaned silver substrate at 25 dyn/cm surface tension: (A) positive ion spectrum, (B) negative ion spectrum.
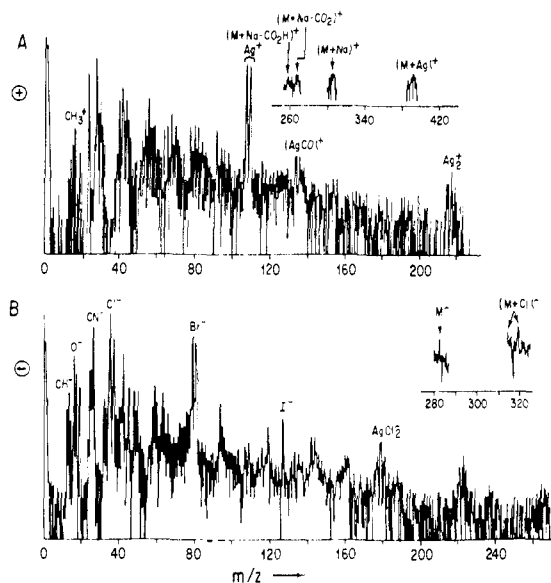
Figure 2. Static SIMS spectrum of a single monolayer of oleic acid prepared and transferred to a clean silver substrate at 25 dyn/cm surface tension: (A) positive ion spectrum, (B) negative ion spectrum.

the carboxyl and alkoxyl oxygens. This is reflected in the results of Table I by noting that all the fatty acids demonstrated M^- and $(M - H)^-$ peaks in their negative ion spectra. Anionization with chloride was observed only for palmitic and oleic acids. No peaks corresponding to Br or I anionization could be detected.

Figure 1 depicts the positive and negative ion SIMS spectra of stearic acid. A series of $(C_nH_m)^+$ fragments is observed (reproducible in group relative intensities) up to $n = 10$. This pattern is characteristic of the positive ion spectra of all the fatty acids studied. One should note that in each individual cluster of ions, odd numbered fragments predominate in intensity.[13-15] This was used as one criteria to distinguish between saturated and unsat-

Figure 3. Static SIMS spectra of a single monolayer of linolenic acid prepared and transferred to a cleaned silver substrate at 25 dyn/cm surface tension: (A) positive ion spectrum, (B) negative ion spectrum.

urated acids. Although the intensity of the peak corresponding to Na^+ is low, Na cationization is observed as well as total decarboxylation of Na cationized stearic acid. No other structure related positive ion fragments were assignable.

In the negative ion spectrum of stearic acid (Figure 1B) various $C_nH_m^-$ and $C_nO_2H_m^-$ fragments are displayed. As in all the spectra, M^- and $(M - H)^-$ peaks dominate the fatty structure assignable features. Cl, Br, and 1 anionization was not observed although these anions were definitely present. Ag^- was seen in various Cl complexes present on the silver surface.

Figure 2 shows the results of positive and negative ion analysis from oleic acid, indicating the signal levels of cationized molecular and deprotonated negative molecular ions. Figure 3 presents the positive and negative ion spectra of linolenic acid, a triunsaturated fatty acid. In the positive ion spectrum (Figure 2A), the same type of pattern of $(C_nH_m)^+$ fragments is observed (up to $n = 10$). Similar features are observed in all other spectra. Only the unsaturated fatty acid spectra demonstrated fairly intense even-numbered fragments (such as m/e 42 and 62) from ion molecule reactions of unsaturated ions. From these data in Figures 2 and 3, it is possible to determine the degree of unsaturation of the fatty acids. Ions due to neutral losses from sodium-cationized molecules are observed. Silver cationization is observed in the positive ion spectrum as are quasi-molecular ions due to neutral losses from the protonated parent ion (such as decarboxylation and loss of HAc). Dimer or higher n-*mer* formation was not observed.

Analysis of the negative ions for linolenic acid (Figure 3B) yields various $C_nH_m^-$ and $C_nO_2H_m^-$ fragments as well as the ubiquitous Cl^- and Br^- peaks. The M^- and $(M - H)^-$ peaks are observed for linolenic acid as for all the other acids. Cl anionization is observed only in the spectra of palmitic and oleic acids. No evidence was seen of Br anionization.

Conclusions

From the foregoing data, it is apparent that static SIMS possesses adequate sensitivity to detect a quantified organized monomolecular layer and to observe molecular and quasi-molecular ions in both positive and negative ion spectra for fatty acids. Also, differences are seen between "gentle" plasma oxidation utilized here and the traditional thick oxide promoting wet

chemical methods[1] in the degree of cationization. Typically, these wet methods produce a high intensity of substrate-cationized quasi-molecular and parent ions. These data support the idea of cationization in these systems as coordination of silver ions to the double bonds in unsaturated acids in the selvage during desorption; the lack of cationization in the saturated fatty acid systems would suggest that silver coordination does not occur at the acid head. Additionally clear differences are observed in relative intensities of quasi-molecular ions between wet oxidized syringe preparations from solution and LB preparations of monolayers. This points out the need to control orientation to understand chemical effects on ion production in SIMS. Because of the high intensities of characteristically even-numbered fragment ions, it is possible to distinguish unsaturation in the monolayer.

Additional research will focus on the influence of cations placed in the trough subphase as matrix assist agents, various substrates such as Au and Cu, surface tension during production, and the examination of Blodgett orientations in multilayers.

Chemical Ionization/Fast-Atom Bombardment Mass Spectrometry: Ion/Molecule Reactions[†]

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Abstract: A novel, high-pressure, fast-atom bombardment (FAB) ion source has been constructed in which ion/molecule reactions of sputtered ions and neutrals can be studied. A variety of ion/molecule reactions are reported on model systems that characterize the important features of this technique. The postdesorption reactions of sputtered species, ions and neutrals, increased the abundance of an $[M + H]^+$ species by almost 3 orders of magnitude. Enhancements in molecular parent ion abundances are shown to result from collisional stabilization, charge-exchange, chemical-ionization, and association reactions. Collisional stabilization of sputtered ions was affected by the different buffer gases, He, Ar, Xe, CO, CO_2, CH_4, and i-C_4H_{10}, and the abundances of molecular parent ions varied in direct proportion to the relative collisional stabilization efficiency of each buffer gas. Results of postdesorption ionization and collisional stabilization are discussed with regard to positive and negative ions of tetraesters and fatty acids.

Introduction

Fast-atom bombardment (FAB) mass spectrometry has proven to be a useful desorption technique for the characterization of intractable chemical species.[1] The FAB mass spectra of involatile middle molecules have yielded both molecular weight and structural information,[2] and many of the major fragmentations in the FAB mass spectra are reported to be similar to those observed by chemical ionization (CI) mass spectrometry.[3] In fast-atom bombardment mass spectrometry (FABMS), secondary ions and neutrals are sputtered from a solid surface, film, molecular overlayer, or a liquid matrix by a primary beam of energetic atoms. Similar emission processes also occur in other particle-induced emission techniques such as secondary ion mass spectrometry (SIMS). The secondary ions, desorbed in these methods, are analyzed by using conventional mass spectrometric techniques.

Several different processes in the particle bombardment process occur yielding various secondary particles. The events include negative and positive ion ejection and desorption of neutral species from the bombarded substrate.[4] The secondary ions and neutral species include molecular species and their fragments and clusters.[5]

The number of sputtered or desorbed neutral organic species should be considerably larger than the number of desorbed mo-

lecular ions. This assumption is based on ion and sputter yields from classical surface studies (metallic substrates) where typical sputter yields (atoms removed/incident particle) range[6] from 0.1 to 10 and positive ion yields (atomic ions/incident particle) range[7] from 1.0 to 1×10^{-4}. Our assumption can be supported and generalized further, based on the results of two studies. The first study showed that typical positive ion yields of organic molecules on a silver substrate (monolayer coverage) are on the order of 5×10^{-2} secondary ions per incident primary particle.[8] The second study demonstrated that ion yields for organic molecules sputtered from a silver surface and from a glycerol matrix are the same order of magnitude.[9] If the molecular neutral yields are significantly greater than the molecular ion yield, as we contend and all the above data indicate, then a simple method for the ionization of the abundant sputtered neutral species will yield increased

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