

Reactive Ion Scattering Spectrometry of Mixed Methyl- and Hydroxy-Terminated Alkanethiolate Self-Assembled Monolayers

Darrin L. Smith, R. Selvan, and Vicki H. Wysocki*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721-0041

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Reactive ion scattering spectrometry (RISS) utilizing low-energy (<100 eV) ion-surface collisions was characterized by using model systems composed of mixed methyl- and hydroxy-terminated self-assembled monolayers (SAMs). Mixed monolayers were prepared by immersing a gold substrate in mixed solutions of dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$; C12- or CH_3 -terminated surface) and 1-hydroxyundecanethiol ($\text{HO}(\text{CH}_2)_{11}\text{SH}$; C11OH- or OH-terminated surface) in tetrahydrofuran or in ethanolic solutions of the unsymmetrical disulfide ($\text{CH}_3(\text{CH}_2)_{11}\text{SS}(\text{CH}_2)_{11}\text{OH}$) for 24 h. The film created from the unsymmetrical disulfide (approximately 50% CH_3 and 50% OH terminating) was used for comparison with the 50:50 film prepared from the mixture of the two corresponding thiols. In a tandem quadrupole instrument, the first quadrupole mass selects ions to collide with the mixed monolayers, and then product ions from the collision are analyzed with the second quadrupole. Benzene molecular ions undergo translational to internal energy conversion (fragmentation), electron transfer (neutralization), and atom/group transfers (ion-surface reactions) upon collision with SAMs. Fragmentation and neutralization observed for benzene molecular ion increase with an increase in the percentage of OH groups present on the surface. The incremental change detected in the relative fragmentation with change in percent composition suggests that H-bonding expected at high %OH does not increase the translational to internal energy conversion detected for the projectile ion at the energies used here; no large "step" change in energy deposition is detected as the %OH is decreased to values that would prevent H-bonding. Benzene molecular ion, $\text{C}_6\text{H}_6^{m/z 78}$, can react with methyl groups to form the reaction product, C_7H_7^+ ($m/z 91$), and its corresponding fragment ion, C_5H_5^+ ($m/z 65$). The methyl abstraction ion-surface reaction product ions can be correlated to the relative concentrations of CH_3 groups in mixed methyl- and hydroxy-terminated SAMs.

Introduction

Self-assembled organic thin films (self-assembled monolayers (SAMs) or Langmuir–Blodgett (LB) films) have been proposed to aid in the development of new technologies, specifically molecular and biosensor devices.^{1–3} Organic thin films are attractive because they can be used to modify the chemical properties of a surface by tailoring the functional groups exposed at an interface. To improve our knowledge of the chemical properties of organic thin films, surface characterization is necessary to determine the chemical composition and structure of the films in addition to understanding the chemistry that occurs at an exposed interface.

One surface characterization technique that provides useful information on the chemical structure and composition of organic thin films is low-energy (<100 eV) ion-surface collisions (reactive ion scattering spectrometry, RISS). Cooks and co-workers and Wysocki and co-workers first reported ion-surface collisions with target surfaces modified with self-assembled monolayers.^{4,5} One result of the ion-surface collision is the dissociative scattering of the incoming projectile ions. This ion activation technique

is known as surface-induced dissociation (SID).^{6–8} Surface-induced dissociation is used in tandem mass spectrometry (MS/MS) experiments and is effective in activation and fragmentation of large biomolecules and other stable molecules.^{9–12} The extent of projectile ion fragmentation has been found to depend on the chemical composition of the SAM target. Fluorinated SAM films have demonstrated a higher conversion of translational energy to internal modes of projectile ions ($T \rightarrow V$) when compared to hydrocarbon films.^{13–16} The increased $T \rightarrow V$ conversion efficiency for fluorinated films compared to hydrocarbon films appears to originate from an increased effective mass of the terminal group ($\text{CH}_3 \rightarrow \text{CF}_3$).^{14,19} Self-assembled

* To whom correspondence should be addressed. Telephone: (520) 621-2628. Fax: (520) 621-8407. E-mail: vwysocki@u.arizona.edu.

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monolayers have also been observed to act as a barrier to electron transfer from the metal surface to the incoming projectile ion in ion-surface collision experiments. The resultant ion signal from ion collisions with surfaces modified with organic films is substantially greater when compared to that from collisions with bare metal surfaces. The degree of ion signal is also dependent on the chemical composition of the ion and organic thin films on a surface; as an example, fluorinated surfaces have provided higher surviving projectile ion current when compared to hydrocarbon surfaces.^{15,17,18} Ion-surface collisions also generate product ions from atom/group transfers between the organic film and the projectile ion. These reaction products are indicative of the chemical composition and structure of the uppermost portion of SAM and LB films.^{14,18–21} Low-energy ion beams have also been applied to the chemical modification of terminal groups of SAMs at the vacuum/film interface.²² Chemical sputtering (including secondary-ion mass spectrometry (SIMS)) has been useful for surface characterization of organic thin films by ionizing and detecting portions of the monolayer chains.^{23–26} However, chemical sputtering is not addressed in the reported low-energy ion-surface collision experiments because it was not a dominant process when low-energy benzene projectile ions were used.

Because low-energy ion-surface collision processes are sensitive to changes in the uppermost portion (primarily the exposed terminal groups) of organic thin films,^{14,19,20} it is logical to consider that these reactions could be used to measure the chemical composition of mixed self-assembled monolayers. The goal of the present study is to characterize low-energy ion-surface collisions (reactive ion scattering spectrometry, RISS) as a surface characterization tool for mixed monolayers with OH and CH₃ terminal groups. The research will determine if ion-surface collision processes (internal energy deposition, electron transfer, atom/group transfer) have the potential to provide qualitative (identifying and monitoring the chemical composition) and quantitative (calculating the relative surface concentrations) analysis of the terminal groups of mixed methyl- and hydroxy-terminated monolayers. Gas-phase benzene projectile ions were utilized for SAM characterization because benzene ions have been extensively studied by RISS and benzene breakdown curves were previously used to generate the extended deconvolution method for calculating the kinetic energy to internal energy conversion ($T \rightarrow V$) during ion-surface collisions.²⁷ The extended deconvolution method has previously determined the energy deposition of benzene ions for ion-surface collisions with other surfaces.^{14,27} Benzene ions have also been shown to be reactive with available CH₃ terminal groups at low collision energies,^{14,18} and they are selective in reacting with the CH₃ groups from the

C12 chains in mixed SAMs. An unsymmetrical disulfide was synthesized and used to generate standard 50/50 methyl- and hydroxy-terminated SAMs. The SAMs generated from the unsymmetrical disulfide were used for comparison to the film prepared from 50/50 C12/C11OH binary solution to establish if the two 50/50 mixed films from different preparations have similar properties.

The mixed monolayer system investigated contains hydrophobic (methyl: CH₃) and hydrophilic (hydroxy: OH) terminal groups. The methyl- and hydroxy-terminated monolayer system has been previously investigated because of the control of surface free energy and chemical affinity that can be achieved.^{28–30} These mixed monolayers are prepared from mixed solutions of dodecanethiol (CH₃(CH₂)₁₁SH) and 1-hydroxyundecanethiol (HO(CH₂)₁₁SH) in tetrahydrofuran (THF) or from the unsymmetrical disulfide (CH₃(CH₂)₁₁SS(CH₂)₁₁OH) in ethanol. Contact angle measurements and X-ray photoelectron spectroscopy (XPS) have shown that the surface concentrations of CH₃ and OH groups are in good agreement with the relative concentrations of dodecanethiol and 1-hydroxyundecanethiol present in THF; that is, %C12 in THF solution \approx surface concentration of CH₃ groups.^{30,31} The solubilities of the two alkanethiols in THF must be comparable to generate m-SAMs that have surface concentrations equivalent to solution concentrations (compared to favored solubility of one thiol in a solvent that causes favored surface adsorption of the other thiol). It has been assumed that the CH₃ and OH groups that are present on the surface exist in a random distribution.^{28,30,32} Scanning tunneling microscopy (STM) research with SAMs produced from ethanolic solutions of the unsymmetrical disulfide CH₃-(CH₂)₁₁SS(CH₂)₁₁OH demonstrated the concentrations of CH₃ and OH groups exist homogeneously at the film interface and are approximately 50% CH₃ and 50% OH.³³

Experimental Section

The alkanethiols [with assigned abbreviations] used in these experiments are CH₃(CH₂)₁₁SH [C12] and HO(CH₂)₁₁SH [C11OH]. The CH₃(CH₂)₁₁SH was used as purchased from Aldrich (99%), and the HO(CH₂)₁₁SH was synthesized and purified from the corresponding alkyl bromide (HO(CH₂)₁₁Br, Sigma (99%)) as previously described.¹⁸ The unsymmetrical disulfide, CH₃(CH₂)₁₁SS(CH₂)₁₁OH [C12-S-S-C11OH], was synthesized and purified using published procedures.³⁴

The vapor-deposited gold surfaces were purchased from Evaporated Metal Films (Ithaca, NY). The gold surfaces consist of a 17 mm \times 13 mm \times 0.5 mm silica base that is covered with a 5 nm adhesion underlayer of titanium followed by 100 nm of vapor deposited gold. The gold surfaces were UV-cleaned for 15 min (Boekel UV cleaner, model 135500, Boekel Industries, Inc.) before immersion in appropriate thiol solutions.

An \sim 1 mM solution of each compound, C12 and C11OH, was prepared in THF. Solutions of C12/C11OH were prepared in various molar percentages (10–100% C12 in solution). Also, a \sim 0.6 mM solution of the C12-S-S-C11OH disulfide in ethanol was prepared to attain a "standard" 50/50 surface. Uniform and mixed monolayers were formed by immersion of a freshly UV-cleaned gold substrate in the appropriate thiol solutions for 24 h. Film formation conditions were based on published procedures

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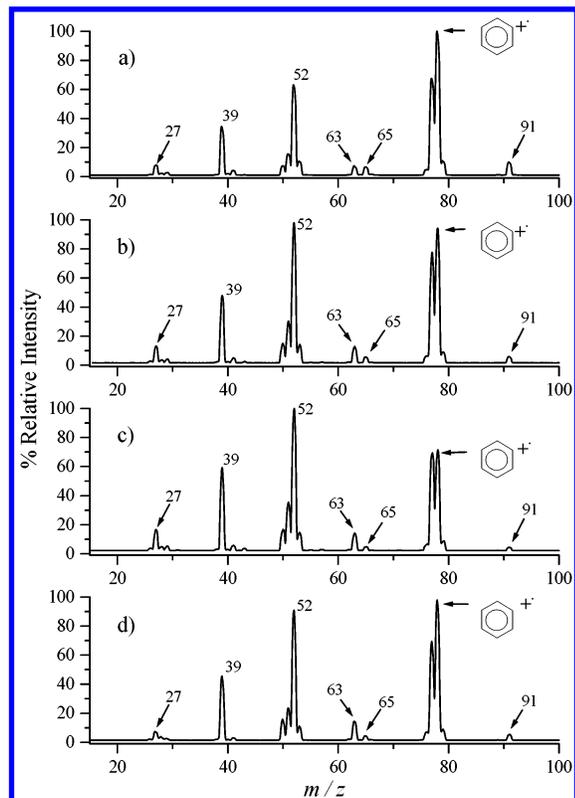


Figure 1. Product ion spectra that result from a 30 eV collision of benzene molecular ion with four C12/C11OH self-assembled monolayers prepared from THF solutions with various molar percentages: (a) 100% C12:0% C11OH; (b) 50% C12:50% C11OH; (c) 25% C12:75% C11OH; (d) the unsymmetrical disulfide (C12-S-S-C11OH) in ethanol.

that generated the previously discussed data;^{30,31,33} that is, XPS and contact angle data demonstrated that the solution concentration of a thiol correlates to the surface concentration of the same thiol. The films were then rinsed six times by sonication in THF (binary thiol solution mixtures) or ethanol (disulfide solutions), dried, and inserted into vacuum through a fast entry lock of the mass spectrometer within 5–10 min.

A description of the basic SID tandem system is published elsewhere.^{14,21} Briefly, two Extrel quadrupole mass analyzers are arranged in a 90° configuration with an adjustable sample holder bisecting the mass analyzers at a 45° angle. Collision energy is controlled by the potential difference between the surface and the ion source; singly charged ions exiting the first quadrupole collide with the organic thin film on the surface. The products of the collision are then focused into and analyzed by the second quadrupole of the tandem system. Ion focusing is accomplished by two sets of three metal lenses, one placed after the first quadrupole and the other placed in front of the second quadrupole (focus ions before and after collisions with the modified surface). A surface holder allows each of four surfaces to be placed in the ion beam successively so that all four surfaces are analyzed under the same experimental conditions. The base pressure of the instrument was 5×10^{-7} Torr, and sample pressure rarely exceeded 9×10^{-7} Torr. Benzene (Aldrich 99+%) projectile ions were generated by 70 eV electron impact.

Results and Discussion

Conversion of Translational Energy to Internal Energy (T → V). Product spectra resulting from a collision between benzene molecular ions (m/z 78) and four different SAMs at 30 eV are shown in Figure 1 (a, uniform C12 SAM; b–d, mixed SAMs from binary solutions and the unsymmetrical disulfide, respectively). By increasing the %OH at the surface (Figure 1a versus 1b versus 1c), the relative abundance of the low mass fragments is enhanced,

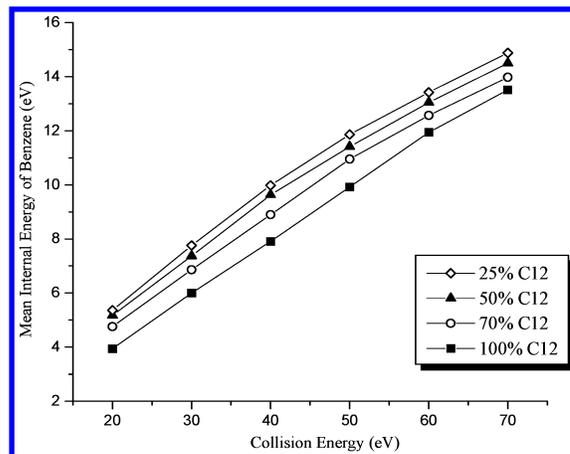


Figure 2. Estimated average internal energy deposited in benzene ion as a function of experimental SID collision energy. Data for a set of mixed C12/C11OH SAMs are compared to data for a dodecanethiol (C12) surface.

Table 1. Average Internal Energy Deposition into Benzene Ion at 50 eV

surface (%C12 in C12/C11OH THF mixtures)	%(T → V) ^a
25%	22.4%
50%	21.7%
70%	20.7%
100%	19.0%
50% (from C12-S-S-C11OH in ethanol)	21.6%

$$^a = [(\text{internal energy})/(\text{kinetic energy})] \times 100\%.$$

signifying an increase in the energy transfer to the projectile ion. The energy transfer characteristics of the films of different chemical composition can be further illustrated for a series of mixed surfaces by using the extended deconvolution method²⁷ to calculate the mean internal energy of benzene for a collection of SID collision energies (Figure 2). The increase of energy deposition to projectile ions is attributed to the effective mass increase of the terminal groups (CH₃ → OH) exposed at the film interface or, because the mass difference is perhaps too small to be consistent with the increase observed, might be the result of different interaction potentials between the ion and the OH surface versus those between the ion and the CH₃ surface.³⁵ This increase of energy deposition has previously been observed with single composition CH₃- and OH-terminated films.³⁶ The relative change in energy conversion from one mixed surface to the next for the mixed SAMs of Figure 2 is approximately 5–9%, a variation sufficient to differentiate between these mixed monolayers. The percentages of kinetic to internal energy conversion for a set of mixed SAMs (calculated from internal energy distribution diagrams for benzene at 50 eV) are shown in Table 1. The T → V efficiency of 19% for 100% C12 is very similar to values calculated, by using the extended deconvolution method, for the energy deposited into benzene colliding with hydrocarbon SAMs.^{14,27} A literature report describing collisions of low-energy argon (0.83 eV) with uniform SAMs reveals that OH-terminated surfaces exhibit different scattering dynamics than CH₃-terminated surfaces.³⁷ This effect is attributed to a more rigid interface resulting from

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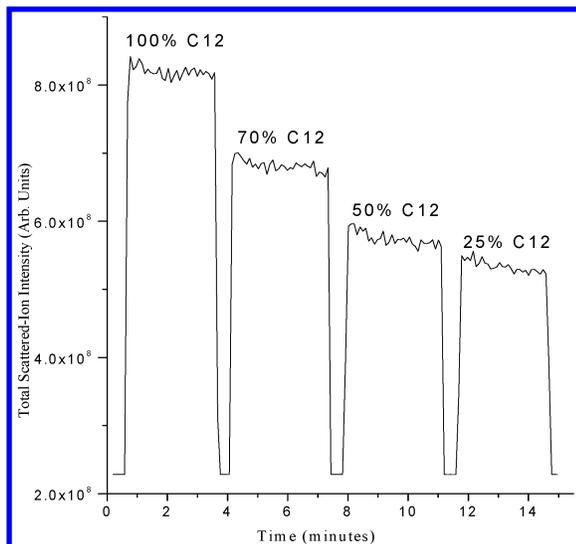


Figure 3. Total surviving scattered-ion current (TIC) measured at the detector of the ion-surface instrument after a 30 eV collision between benzene ions and a set of C12/C11OH mixed SAM films formed from THF binary thiol solutions (molar percentage indicated).

hydrogen bonding between OH.³⁷ Data reported for mixed SAMs consisting of a 1:1 ratio of OH- and CH₃-terminated thiols of equal chain length suggest a completely disrupted hydrogen-bonding pattern.²⁸ The calculated average energy deposition presented for these mixed SAMs (Figure 2) increments with the %C11OH rather than abruptly changing in a manner that would be expected if a composition is reached that disrupts H-bonding. This leads to the conclusion that the change in energy deposition is not dependent on hydrogen bonding at the interface (unlikely to remain intact at the energies of our collisions) but dependent on some other parameter such as the change in effective mass of the terminal group or different interaction potentials. The ion-surface spectra of Figure 1b and d have similar characteristics and the corresponding calculated energy deposition values are in good agreement (Table 1). These data support the previously reported conclusion that the terminal group composition of the two films is approximately 50% CH₃ and 50% OH.^{30,31,33} There have been a variety of methods developed that can be used to estimate the amount of internal energy deposited,^{7,16,38,39} however, the goal of this study was to compare the energy deposition differences for the mixed films, so other estimation methods will not be presented.

Changes in Electron Transfer. A plot of relative electron transfer for a set of methyl- and hydroxy-terminated mixed films using benzene molecular ion incident at 30 eV is presented in Figure 3. The total ion current (TIC) presented (*y*-axis) is a measure of the total scattered ions detected at the electron multiplier (without neutralization) after surviving the collision with the modified surface. The total ions that can survive include the projectile, fragment, and reaction ions, that is, all the ions that appear in the tandem mass spectrum (Figure 1). The baseline in Figure 3 was achieved when the ion source filaments were turned off, that is, when no ions collided with the surface. An increase in the percentage of OH groups on the surface results in a decrease in the surviving ion current and a corresponding increase in the extent of

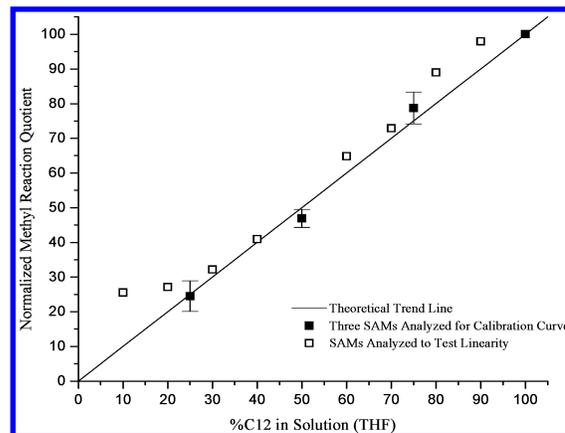


Figure 4. Plot correlating the methyl reaction quotient (MRQ) to the %C12 in solution (surface concentration of CH₃ groups) for quantitation of C12/C11OH mixed SAMs using benzene (30 eV kinetic energy). The trend line shown is the theoretical line for an ideal calibration curve between the normalized MRQ and molar %C12 in solution ($R = 1.000$). Error bars represent the experimentally determined standard deviation for data acquired from the three mixed SAMs.

neutralization. This result is consistent with research where OH-terminated surfaces cause more neutralization of benzene and pyrazine ions when compared to uniform hydrocarbon surfaces.⁴⁰ The mechanism of electron transfer during low-energy ion-surface collisions for CH₃- and OH-terminated SAMs is still being investigated.⁴⁰ The measurable, predictable decrease in neutralization with increasing percentages of OH groups present at the surface might prove useful for quantification of mixed methyl- and hydroxy-terminated films or other similar mixed films where the identity of the surface terminal groups is known but the percentage of each component needs to be characterized.

Ion-Surface Reactions with Mixed Methyl- and Hydroxy-Terminated SAMs. In addition to the energy transfer and electron transfer differences for ion-surface collisions with mixed SAMs, reaction products of benzene ions with mixed methyl- and hydroxy-terminated monolayers were utilized to detect changes in the percentage of CH₃-terminal groups at the SAM interface. Benzene molecular ions (*m/z* 78) colliding with CH₃-terminated SAMs have been shown to produce reaction product ions, C₆H₆^{•+} + CH₃ - H₂ = C₇H₇⁺ (*m/z* 91), some of which gain enough internal energy to fragment to C₅H₅⁺ (*m/z* 65).¹⁸ To determine differences in the reaction products for a series of mixed surfaces, a methyl reaction quotient was generated. The methyl reaction quotient (MRQ) is defined as the sum of the ion-surface reaction product peak areas divided by the sum of the total peak areas present in the spectrum: % methyl reaction quotient (MRQ) = [(C₇H₇⁺ = *m/z* 91) + (C₅H₅⁺ = *m/z* 65)]/total peak area × 100%. The methyl reaction quotient was then normalized to a reference surface (a 100% C12 SAM was included in each set of four samples) so multiple surfaces could be compared. The correlation between 25%, 50%, 75%, and 100% C12 in solution (or surface concentration of CH₃ groups) and the normalized methyl reaction quotient is illustrated in Figure 4 (closed symbols). Each data point represents an average of measurements from three independent surfaces with an experimentally determined standard deviation. The independent SAMs were prepared on different days from different solution mixtures. The data point at 100% C12 does not have error bars because this was the reference

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point for normalization of the other mixed monolayers. The plot clearly demonstrates that ion-surface reactions generate a calibration curve for possible quantitation of mixed monolayers with a linear dynamic range from 25% to 100% C12. The line drawn in Figure 4 is the theoretical line for a perfect calibration curve between the normalized methyl reaction quotient for a 100% C12 film extended down to 0. The correlation coefficient for the four average points was calculated to be 0.997. The calculated average MRQ for the 50% methyl- and hydroxy-terminated surface from the THF solution is 46.9%, and the calculated average MRQ for the 50% methyl- and hydroxy-terminated surface from the disulfide is 48.2%. This agreement for the two 50:50 methyl-/hydroxyl-terminated surfaces further supports the similarity of the two surfaces compositions, consistent with each possessing an approximate 50% mixed surface composition of CH₃ and OH groups. To test the limits of the ion-surface quantitation method, a set of surfaces with smaller increments of C12 in solution (CH₃ groups at the surface) were analyzed. The methyl reaction quotients from the mixed surfaces ranging from 10 to 90% C12 in solution are also shown in Figure 4 (open symbols). Linearity was preserved between at least 30 and 70% C12, suggesting that reactive ion scattering spectrometry can be used to differentiate methyl and hydroxy mixed surfaces over this range of compositions.

Deviations from the theoretical line are observed for surfaces prepared from higher concentrations of C12 in solution, particularly 80–90% C12. Ion-surface reaction results for 90% and 100% C12 surfaces are similar. Either a small percentage of OH-terminated chains (10% OH for the 90% C12 surface) is not enough to effectively change the interface that the benzene ion beam samples (the ion beam samples similar vacuum/film interfaces, resulting in similar MRQ values) or the 10:90 OH:CH₃ films do not consist of the same OH percentage as that of the mixture from which they were prepared. Another area that deviates from the linear portion of the plot is at lower concentrations of C12 chains (10% and 20% C12). At lower concentrations of C12, deviation from linearity from the theoretical line could be explained by two additional reactions that could occur with the C11OH film. The appearance of the ion-surface reaction products that typically correspond to methyl addition (*m/z* 91 and 65) is apparent on 100% C11OH films (spectrum not shown). These product ions could be produced from reaction of benzene ion either with physisorbed hydrocarbon contamination or with the upper portion of the C11OH film (C₆H₆⁺⁺ + –CH₂OH (from film) → C₇H₃O⁺ → –H₂O → C₇H₇⁺ (91)). Previous research found that OH groups in a 50% CH₃ and 50% OH mixed monolayer are slightly lower in the film surface plane than CH₃ groups (0.1 ± 0.02 nm).³³ As the more exposed CH₃ groups become less available with increasing additions of C11OH thiol to the solution mixture, the projectile ion can interact more with the C11OH chains in the mixed films. The deviation seen at low %C12 could result from a surface composition at higher concentrations of C11OH in solution (10% and 20% C12) that is higher in C11OH than would be predicted from equal adsorption of the two thiols, but this explanation is in conflict with reports in the literature.³⁰ Reaction products from (+CH₂OH –H₂O) addition at high C11OH surface concentrations would falsely increase the numerator of the MRQ equation, thereby giving MRQ values higher than expected. At low concentrations of C12 in the mixed monolayer SAMs, a baseline MRQ is established from reaction of benzene projectile ion with underlying methylene from the C11OH chains (e.g., (+CH₂OH –H₂O) addition resulting in the same formal methyne (CH) addition as (CH₃–H₂) addition

on alkyl-terminated films) and/or physisorbed hydrocarbon contamination. Until the CH₃ group concentration on the surface (%C12 in solution) is higher or more available than these “noise” components, there is no linear correlation between the MRQ and the surface composition (plateau region in Figure 4 at low concentrations of C12). These additional reaction pathways could be investigated with isotopically labeled C11OH films (where the methylene under the terminal group is deuterated; currently not available) or with deuterated C12 (corrected for isotope effect) and/or with an improved vacuum system. Despite the reactivity of the OH films at high OH concentrations in the film, the methyl reaction quotient from benzene ion-surface reactions provides a linear dynamic range from 30 to 70% C12 that can differentiate C12/C11OH (methyl- and hydroxyl-terminated) mixed surfaces from each other.

Conclusions

Several authors, using a variety of experimental methods, have previously characterized mixed SAM films with varying percentages of OH and CH₃ at the air/film or vacuum/film interface. In the research presented here, model mixed methyl- and hydroxy-terminated SAM surfaces were used to probe the usefulness of reactive ion scattering spectrometry (RISS), which involves low-energy ion-surface collisions, as a surface characterization tool. The extent of fragmentation and neutralization detected upon ion collision at the films changes with the composition of C12/C11OH mixed films. The abstraction of available CH₃ groups from the C12 chains of C12/C11OH mixed monolayers by benzene projectile ions was examined. A calibration curve was generated by plotting the methyl reaction quotient versus the %C12 in solution (concentration of CH₃ groups on the surface). Additional reaction products from other possible sources (C11OH terminal groups or hydrocarbon contamination) limit the quantitation method. Linearity was preserved for surfaces prepared from 30 to 70% C12 in solution. Results from ion-surface collision processes (internal energy deposition and ion-surface reaction) validate that a 50% CH₃- and 50% OH-terminated SAM surface was created both from a mixture of the two thiols in THF and from the unsymmetrical disulfide. RISS was not shown by this work to have particular advantages over other surface characterization tools (such as FTIR or XPS or laser desorption MS⁴¹) in characterization of %OH or %CH₃, but it was shown to provide results consistent with those of the more established surface characterization tools. One piece of data that is available from RISS that is not available from surface spectroscopies or laser desorption MS is the nature of the surface as a “hard” or “soft” collision target for projectile ions. The increased T → V efficiency of the mixed monolayers with higher %OH is attributed to an effective mass increase of the known terminal groups (CH₃ → OH) or to differences in the interaction potentials between the projectile ion and different surfaces, but not to the presence of possible hydrogen bonding on the surface. These results will be useful as computational models of ion-surface energy transfer are further refined.

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