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Investigation of tribo-chemistry by means of stable isotopic tracers: TOF-SIMS analysis of Langmuir–Blodgett films and examination of their tribological properties

I. Minami, T. Kubo, S. Fujiwara, Y. Ogasawara, H. Nanao and S. Mori*

Department of Chemical Engineering, Iwate University, Ueda 4-3-5, Morioka, Iwate 020-8551, Japan

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Deuterium-substituted and ^{13}C-substituted octadecanoic acids were applied to study tribo-chemistry of binary-component Langmuir–Blodgett film deposited on Si(100) surfaces. Time-of-flight secondary ion mass spectroscopy was employed to study structure of the film. The isotopic tracers give typical fragment ions composed of the isotopes. Among these typical fragment ions, we paid attention to quasi-molecular ions and deuterium ion as "fingerprint region" of the film structure. The tribological properties of the binary-component film were evaluated by ball-on-plate type tribo-testers. The combination of octadecanol with octadecanoic acid affords good tribological properties, whereas the combination of octadecylamine with the acid gave poor results. The surface analysis of the plate after the tribo-test revealed that the alcohol and the acid were retained on the track even after the rubbing. On the other hand simultaneous removal of the acid and the amine from the surfaces were observed. Interactions between the acid and the amine were considered by the results of the tribo-tests and the surface analysis of the binary-component film.

KEY WORDS: time-of-flight secondary ion mass spectroscopy, perdeuteriocarboxylic acid, inactive tracer, monolayer organic film, binary additive system, boundary lubrication conditions, friction modifiers, Langmuir–Blodgett films

1. Introduction

Surfactant type friction modifiers such as higher fatty acids are well known to reduce wear and friction under mild boundary conditions [1]. Their tribological properties based on structure of the acid had been well studied using the Langmuir–Blodgett (abbreviated to LB hereafter) film as a model of boundary film. At present, their lubrication mechanisms are generally explained by a close-packed film composed of oriented molecule on the rubbing surface; thereby prevents metal-metal contact [2–8]. Importance of two-dimensional elastic modules of LB type film is also pointed out [9].

In our preliminary work on the tribological properties of LB type film, synergism and antagonism in binary-component LB film system were observed. Surface analysis of the boundary film would contribute to understand the mechanism for combination. To date, electron probe microanalysis, X-ray photoelectron spectroscopy, and Auger electron spectroscopy have been widely applied in tribo-chemistry [10]. These techniques show many advantages to provide chemical information of heteroatom-derived compounds such as metal sulfides and metal phosphates. Usually precursors of LB films are composed of a long-chain hydrocarbon moiety and a hetero-atom-containing functional group. Only a small amount of the hetero-atom exists in LB films. Therefore detection of these elements is not always satisfactorily even by a high sensitive analysis. In addition, it is not easy to detect higher fatty acids separately from organic contaminants. Tribo-chemistry of carboxylic acids has been studied by X-ray adsorption spectroscopy [11–12], by infrared spectroscopy [13] and by Raman spectroscopy [14]. However, these techniques seem not suitable to obtain chemical information of binary-component LB film.

Recently, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) was introduced as a sophisticated surface analysis technique for tribological surfaces [15–23]. The outline of the analysis is based on mass spectrum of compounds which exist on the surfaces. Advantages of this method in tribo-chemistry are high sensitivity, high spatial resolutions, and excellent chemical resolutions if fragmentation of molecule was well studied. Therefore, both organic and inorganic compounds on the surfaces are detectable by TOF-SIMS. In addition, isotopes in a target molecule can be identified by the high-mass-resolution technique of TOF-SIMS [24]. Isotopes are defined as atoms having the same atomic number but a different mass number. They exhibit different physical properties but the same chemical ones. Both radio-active isotopes and inactive ones (namely, stable isotopes) are found in natural resources [25]. Some of them are applied as tracers to study metabolism or terrestrial ecosystem [26]. In the field of tribology, applications of radio isotopes of

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*To whom correspondence should be addressed.
E-mail: mori@iwate-u.ac.jp

hetero-atoms have been reported to trace boundary film formation [27] and wear measurement [28]. Although radio isotopes are easy to detect even at low concentrations in the system, they might make the researchers aware of the radiation damages. Therefore, handlings of them are limited by legislations.

Taking these backgrounds into account, our attention was focused on application of stable isotopic tracers in tribo-chemistry of binary-component LB film. Our model is based on labeling of hydrocarbon moiety in LB film precursors; thereon chemical analysis of rubbed-surface by TOF-SIMS. Features of the model system are to perform direct analysis of hydrocarbon moiety in a lubricant, which contains a lot of organic compounds.

2. Experimental

2.1. Chemicals and preparation of the boundary film

2,2–Dideuteriooctadecanoic acid (n-$C_{17}H_{33}$ CD_2 COOH), octadecanoic acid-1-^{13}C (n-$C_{17}H_{35}{}^{13}$ COOH), pentatriacontadeuteriooctadecanoic acid (n-$C_{17}D_{35}$ COOH, abbreviated to COOH hereafter) were selected as stable isotopic tracers for the present work. Octadecanoic acid (n-$C_{17}H_{35}COOH$) was also examined as a reference. Octadecanol (n-$C_{18}H_{37}OH$, abbreviated to OH hereafter) and octadecylamine (n-$C_{18}H_{37}NH_2$, abbreviated to NH hereafter) were selected as a co-precursor of the boundary film. All chemicals are reagent grade.

The Langmuir–Blodgett type boundary film was deposited on Si(100) flat surface using a computer-controlled Langmuir trough under air [9]. Equimolar solution of the binary precursors (1 mmol/dm^3 of each component) in chloroform was spread uniformly over anaqueous solution of barium chloride (3×10^{-2} mmol/dm^3) composed of potassium bicarbonate (0.4 mmol/dm^3) as pH buffer. The temperature of the trough was 20.0 ± 0.1 °C. The organic solvent was allowed for evaporation at least 30 min, and then films were compressed at a rate of 0.1 mm/s. Deposition speed of all the monolayers was 1 mm/min. The Si plate was rinsed in benzene-ethanol solution and ultrapure water in succession in an ultrasonic bath. In order to remove surface organic contaminants, the substrate was treated under ozone for 20 min prior to use.

The surface free energy of the film was calculated from the results of static contact angles of distilled water and diiodomethane on the film surfaces. The surface free energy of the film deposited from OH + COOH and NH + COOH were 52.8 and 54.0 mJ/m^2, respectively.

2.2. TOF-SIMS analysis

The TOF-SIMS measurements were performed with a Physical Electronics TFS-2100 (TRIFT-II) instrument. High mass resolution spectra of $M/\Delta M > 5000$ at m/z 26.98 (Al) were acquired using bunched Ga$^+$ ion pulses with an impact energy of 15 keV, an ion current of 2 nA for one pulse, a pulse width of 7 ns (960 ps after bunching) and a pulse frequency of 11 kHz. The measured mass range was m/z 1–3000. Total ion doses in these measurements were $< 1 \times 10^{12}$ ions cm^{-2}. Both positive ions and negative ions were detected. Area of analysis for chemical mapping was 180 μm × 180 μm. The TOF-SIMS spectra were obtained for the friction surfaces after lubrication tests, and for the LB film deposited on Si(100) surfaces. The measurements were performed on two positions of area which includes both rubbed-surfaces and unrubbed-surfaces, in order to confirm reproducibility. Both negative and positive ions were detected. An area of analysis covers both inside and outside of the wear track as expressed in figure 1. Therefore we can compare the distribution of compounds by studying chemical mapping of these areas. Relative concentrations of compounds were taken into account by comparing intensity of individual fragments detected both on worn surfaces and on outside of the track.

2.3. Tribo-test

A stainless-steel-ball on rotating-plate type tribo-tester was employed to compare durability of the film on the plate. A load of 1 N and sliding velocity of 2.2 mm/s were applied. Tribological properties of the film at initial stage were examined by a glass-ball on sliding-plate type tribo-tester. A load of 40 mN and sliding velocity of 0.02 mm/s were applied.

3. Results and discussion

3.1. TOF-SIMS analysis of the stable isotopic tracers

Quasi-molecular ions of octadecanoic acids in TOF-SIMS spectra are shown in figures 2–5. Here we define M as formula weight of the original acid. In all negative

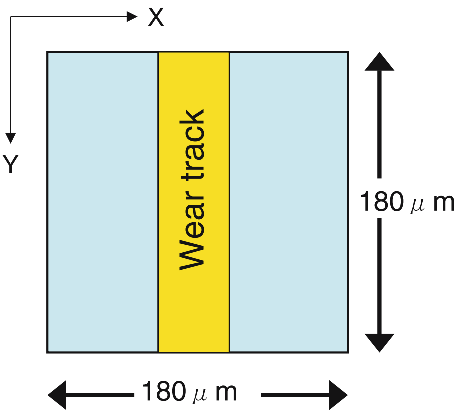

Figure 1. Area of TOF-SIMS analysis for chemical mapping.

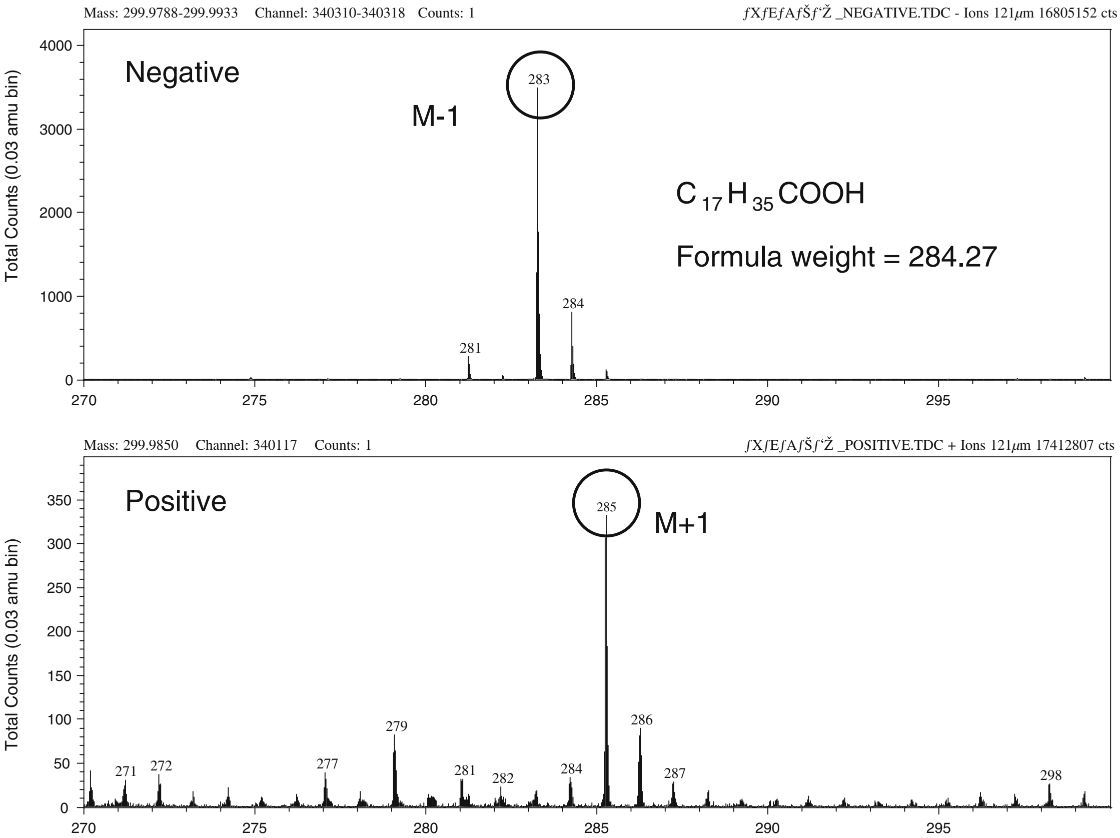

Figure 2. TOF-SIMS spectra of $C_{17}H_{35}COOH$ (*m/z* 270–300).

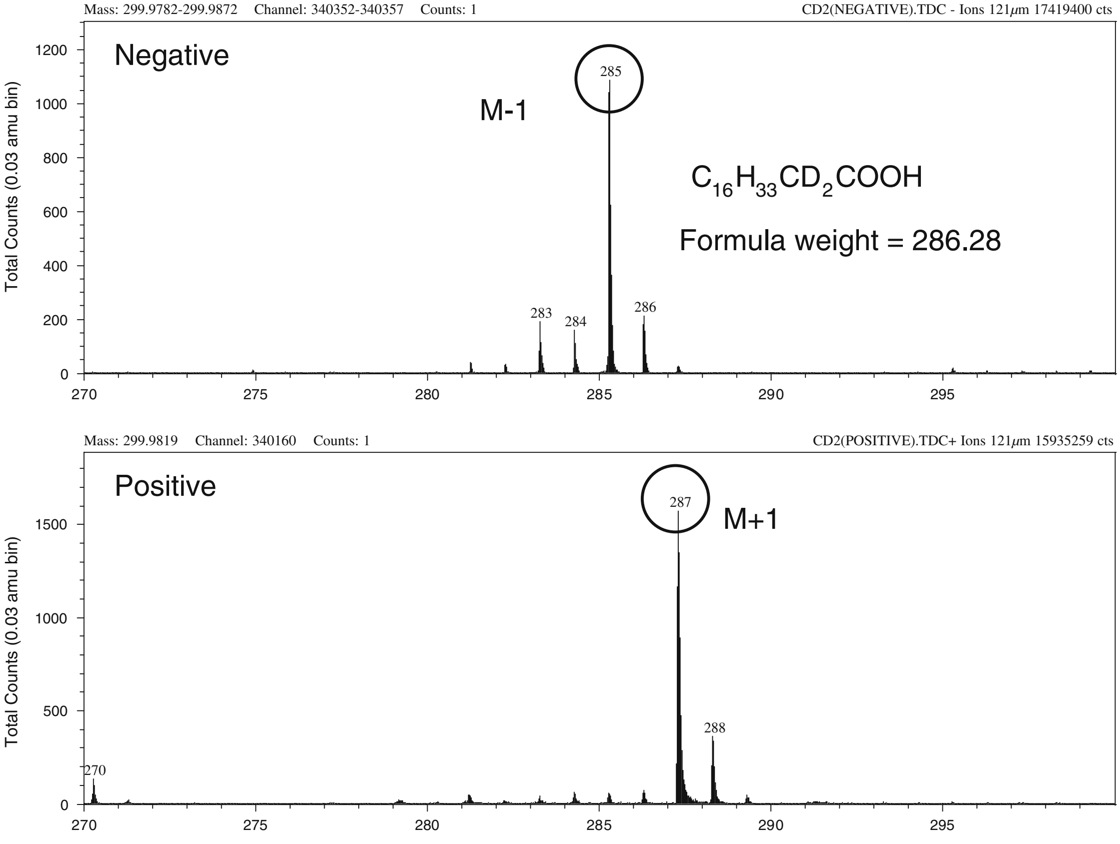

Figure 3. TOF-SIMS spectra of $C_{16}H_{33}CD_2COOH$ (*m/z* 270–300).

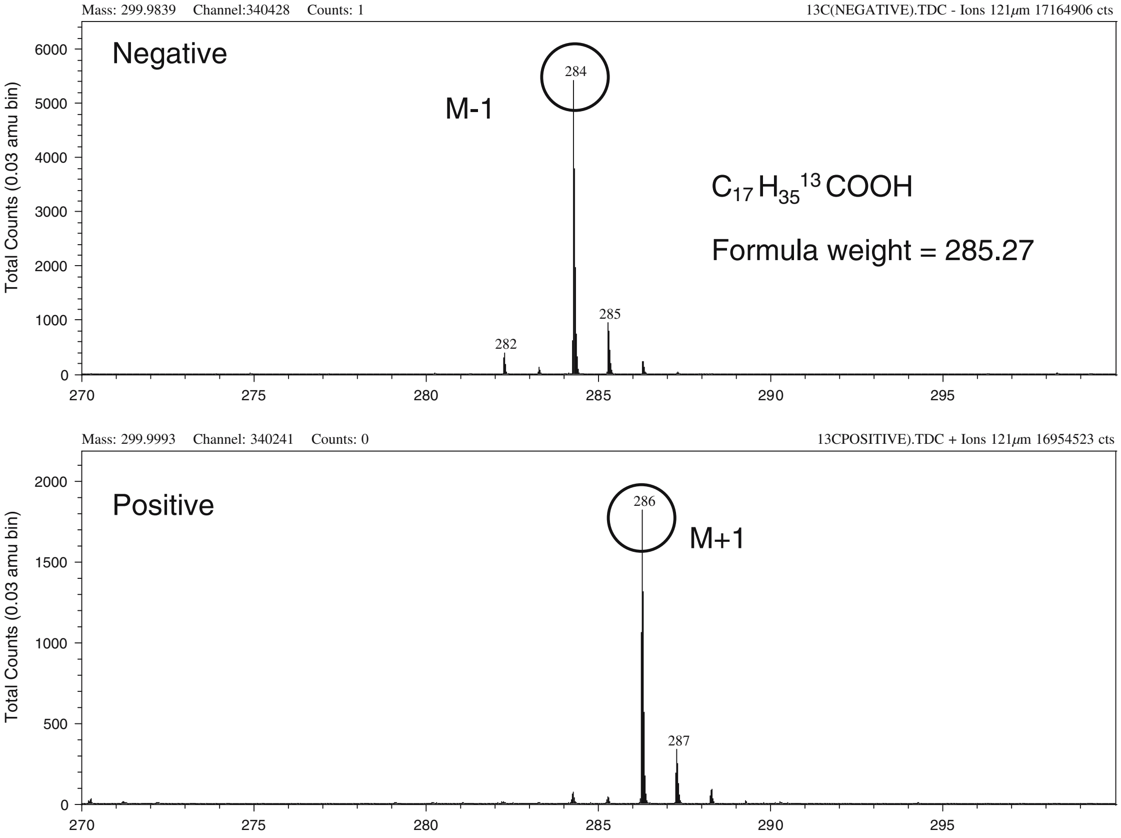

Figure 4. TOF-SIMS spectra of $C_{17}H_{35}{}^{13}COOH$ (*m*/*z* 270–300).

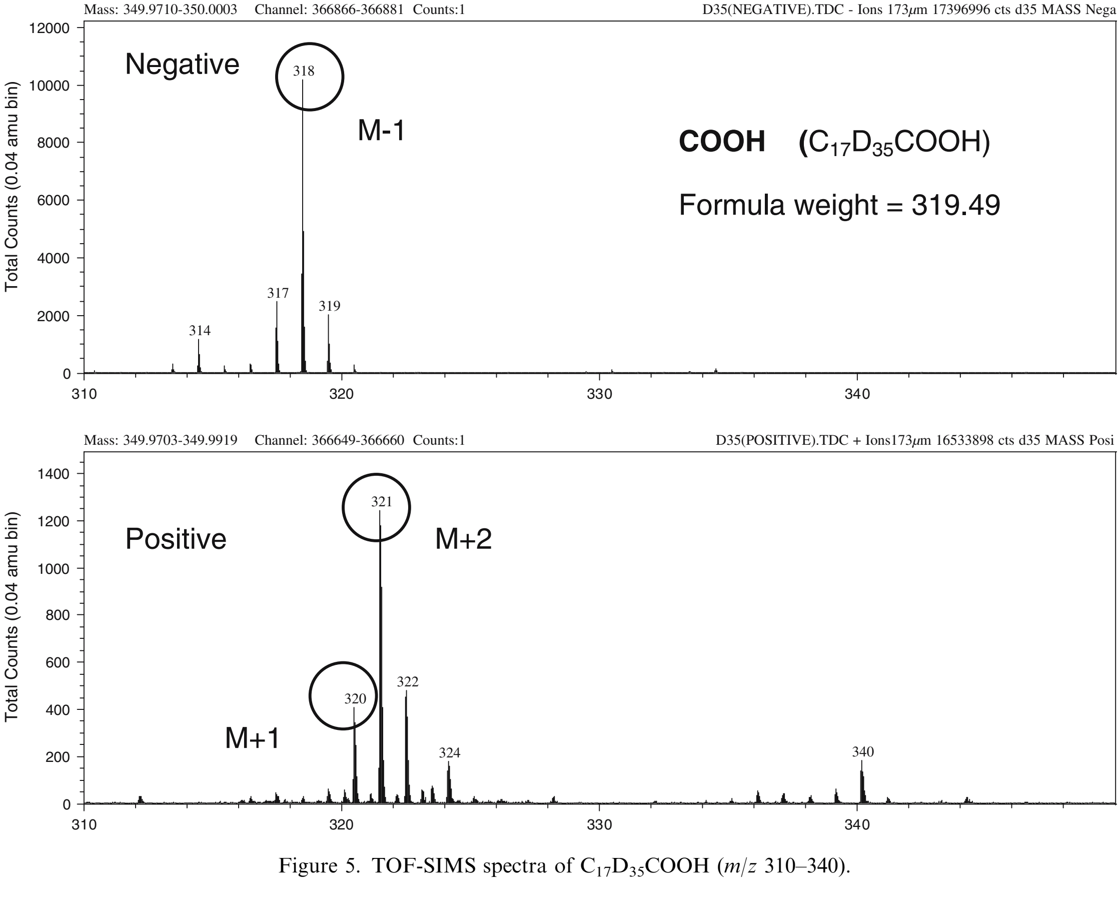

Figure 5. TOF-SIMS spectra of $C_{17}D_{35}COOH$ (*m*/*z* 310–340).

spectra, mass-to-charge ratio (abbreviated to *m/z* hereafter) of $M-1$ is clearly observed. The results can be understood by the migration of a proton (hydrogen cation, *m/z* 1) from the original acid to give carboxlate anion. We found clear differences in the positive ion spectra depending on distribution of isotopes in the molecule, as expressed in figures 2–5. COOH affords *m/z* $M+2$ as the major quasi-molecular ion whereas other acids gave *m/z* $M+1$ as the major one. The formation of the quasi-molecular ion of *m/z* $M+1$ can be understood by the reaction of a proton with the original acid, as expressed by figure 6. Similarly, the quasi-molecular ion of *m/z* $M+2$ is formed by the reaction of a deuteron (deuterium cation, *m/z* 2) with the original acid. Since COOH molecule is composed of 35 deuterium atoms in the alkyl moiety and one hydrogen atom in the carboylic moiety, there are much more possibility to generate deuteron than proton during the fragmentation of COOH. As the results, quasi-molecular ion of *m/z* $M+2$ was obtained in preference to that of $M+1$.

Taking the results discussed above, COOH whose alkyl group is completely substituted by deuterium, seem to be appropriate tracer molecule. Typical fragment ions from the tracer were also observed. As examples, negative and positive spectrum of COOH in the low mass range (*m/z* 0–20) is compared with those of *n*-$C_{17}H_{35}COOH$, as shown in figures 7–8. Strong signal of *m/z* 2 attributed to deuterium was found in both negative and positive spectrum. In addition, *m/z* 14 and 18 were found. These fragment ions were not found in the spectra of the normal acid, *n*-$C_{17}H_{35}COOH$ at all. Therefore the fragment ions have deuterium atom. For these fragment ions, CD and OD are most reliable. The positive spectra show typical fragmentation of alkyl group clearly. *n*-$C_{17}H_{35}COOH$ affords fragment ions of *m/z* 12–15 at the intervals of 1. They correspond to C, CH, CH_2, and CH_3, respectively. Obviously, COOH gives fragment ions of *m/z* 12–18 at the intervals of 2, which correspond to C, CD, CD_2, and CD_3, respectively. Among these fragment ions, negative ions of *m/z* 2, 14, 18 and positive ions of *m/z* 2, 16, 18 are found only in the spectrum of COOH.

Careful study of TOF-SIMS spectra of COOH affords the fragmentation of the tracer molecule in detail. For example, positive spectra of COOH at *m/z* 200–330 shows the typical fragment ions at the intervals of 16, as shown in figure 11 briefly. The fragment ion of *m/z* 211.94 was found by a high resolution mass spectrum (not shown here), which can be identified as $C_3D_3O_2Ba$. Therefore, the series of the fragment ions at the intervals of 16, namely $C_nD_{2n-3}O_2Ba$, indicate the presence of barium salt of COOH on the surfaces. Since hydrogen (*m/z* 1) is found in both negative and positive spectrum in figures 7–8, we considered that the LB film is composed of the free acid and the barium salt.

In consequence, several fragment ions inherent to COOH were clarified. We wish to propose that these fragment ions and quasi-molecular ions of $M+2$ have potential to be "fingerprint region" of the tracer, COOH.

3.2. *TOF-SIMS analysis of binary-component LB film*

Intensities of positive quasi-molecular ions of $M+1$ and $M+2$ became almost equal when a binary-component LB film was analyzed by TOF-SIMS, as shown in figure 9. The results can be well understood by the generation of both proton and deuteron from the precursors. On the other hand, we could not find any differences in negative spectrum of quasi-molecular ions between single-component LB film and binary-component one. It should be pointed out that intensities of negative ions are much higher than those of positive ones.

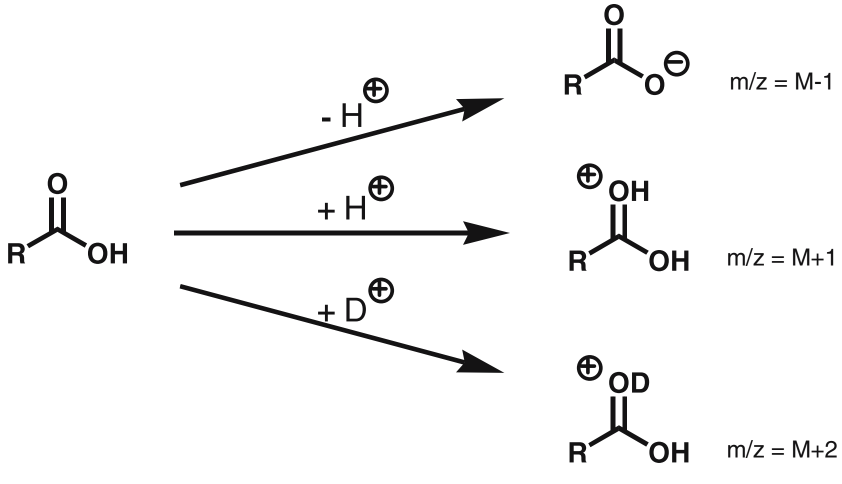

Figure 6. Generation of quasi-molecular ions from carboxylic acids.

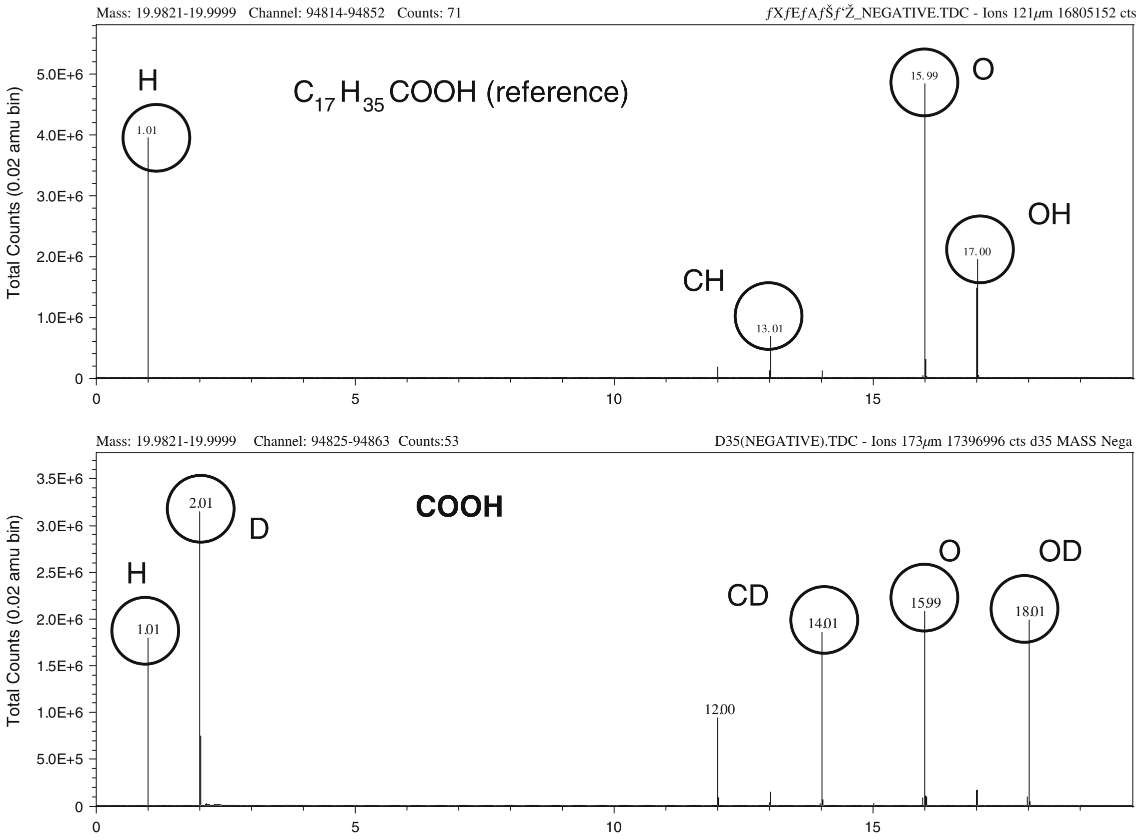

Figure 7. TOF-SIMS spectra of $C_{17}D_{35}COOH$ (m/z = 0–20, Negative).

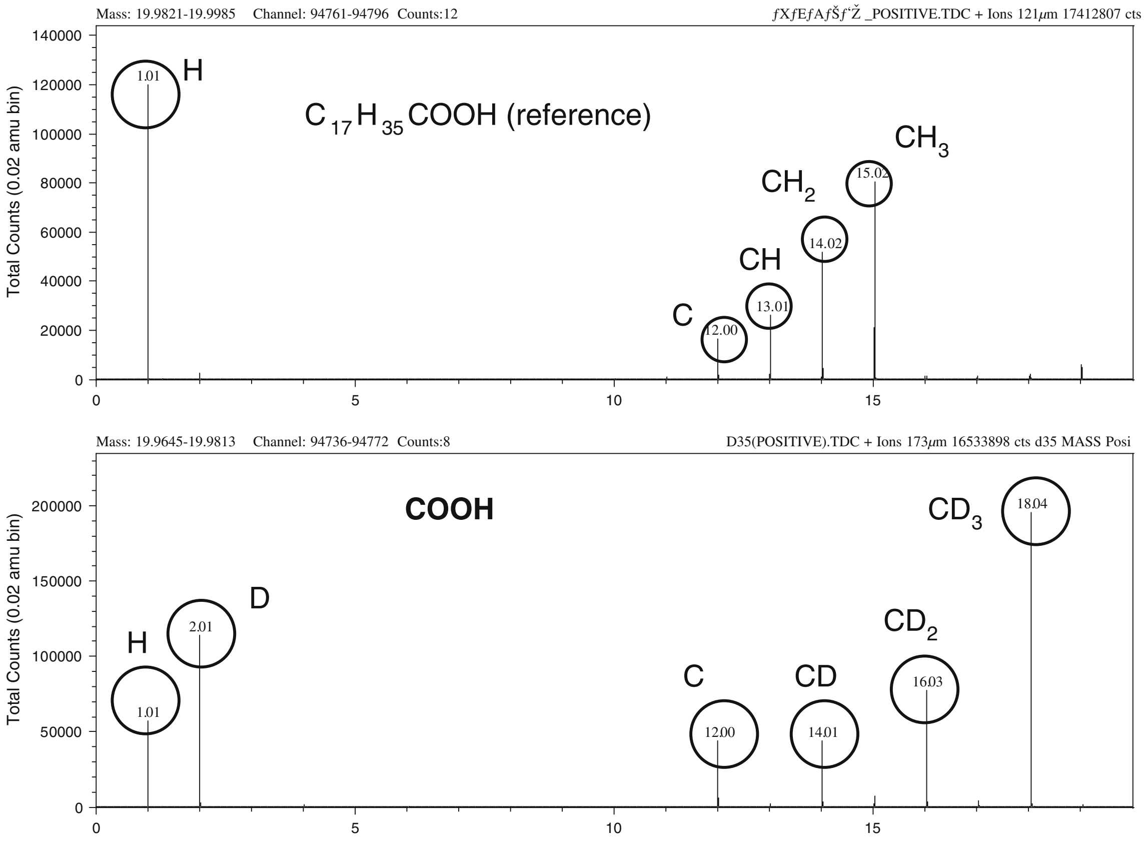

Figure 8. TOF-SIMS spectra of $C_{17}D_{35}COOH$ (m/z = 0–20, Positive).

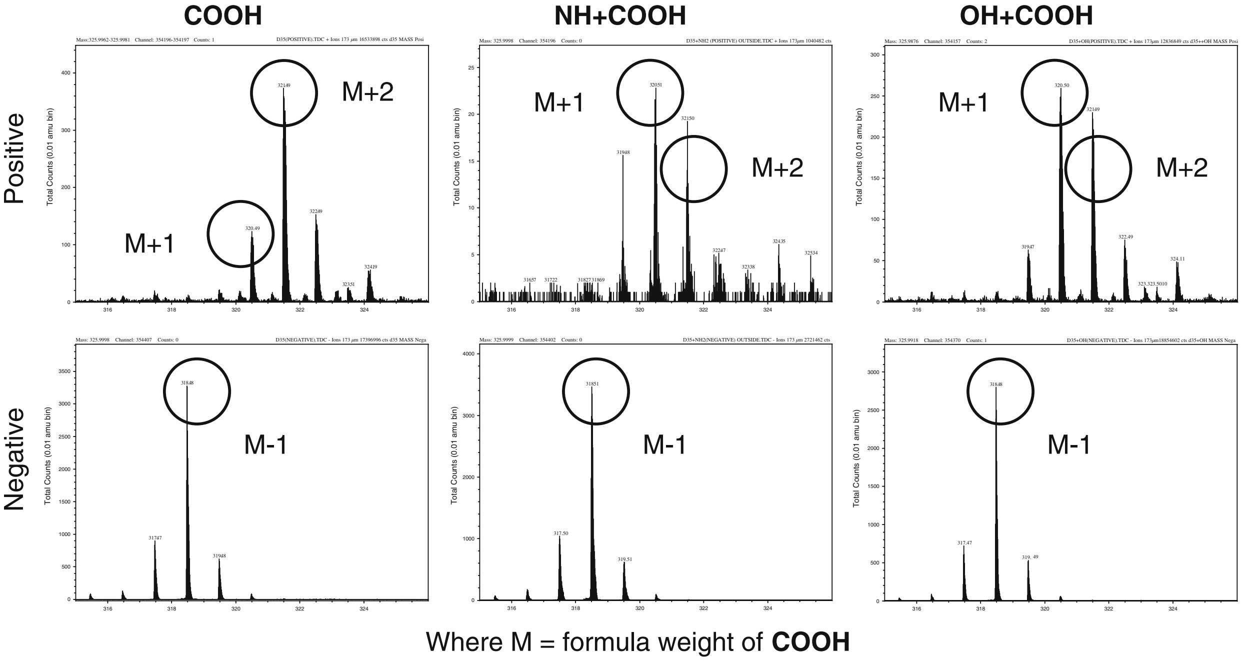

Figure 9. TOF-SIMS spectra of binary LB film (Quasi-molecular ions).

As mentioned above, the LB film of COOH is composed of barium salt. The migration of the metal from the salt affords carboxylate anion which can be detected as *m*/*z* *M*–1 as negative anion. Formation of positive quasi-molecule ions requires two-step recombination from the salt; namely, reaction of carbolylate anion with proton (or deuteron) to afford the original acid followed by the second protonation (or deuteronation), as expressed in figure 10. The intermediates, RCO_2H or RCO_2D have no charges. Therefore they are inactive species for the TOF-SIMS analysis. Positive quasi-molecule ions *m*/*z* $M+3$ were also detected, however the intensities of them were extremely low compared to those of *m*/*z* $M+1$ and *m*/*z* $M+2$. Therefore we took quasi-molecule ions of $M+1$ and $M+2$ into account. Anyhow, due to the series of the reactions, the amount of positive quasi-molecular ions from the salt might be lower than that of negative ones.

Taking the assumption into account, we compare the ratio of positive ($M+1$ and $M+2$) and negative (*M*–1) ions as sown in table 1. Intensities of these ions were

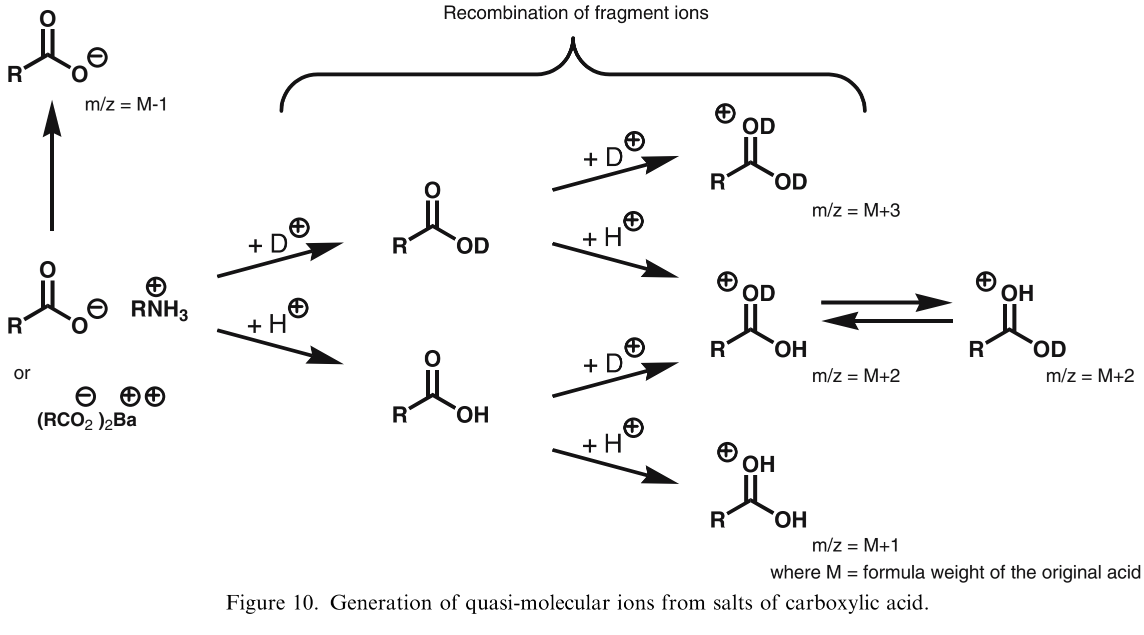

Figure 10. Generation of quasi-molecular ions from salts of carboxylic acid.

Table 1.
Ratio of positive quasi-molecular ions and negative quasi-molecular ion.

	Positive		Negative m/z 318 ($M-1$)	Positive/ Negative ratio
	m/z 320 ($M+1$)	m/z 321 ($M+2$)		
COOH	7.9E-05	2.6E-04	1.2E-03	0.28
NH + COOH	2.1E-04	1.5E-04	1.0E-02	0.036
OH + COOH	2.2E-04	1.8E-04	8.5E-04	0.47

normalized by the intensity of the total ions. The ratio of positive ions to negative ions decreases by an order when the film was deposited from NH + COOH. The results suggest that much more carboxylate anion was formed on the surfaces. In fact, reaction of amines with carboxylic acids affords corresponding salts [29].

The fragment ions attributed to $(C_nD_{2n-3}O_2)_2Ba$ were also found in the TOF-SIMS spectrum of the binary-component systems. However the intensities of the fragment ions, especially in the spectra of NH + COOH are too low to identify clearly (figure 11).

3.3. Tribological properties of binary-component LB film

Results of friction trace during the ball-on-rotating-flat test with the binary-component LB film are shown in figure 12. Friction coefficient with NH + COOH increases after approximately 100-s of rubbing. On the other hand, steady friction coefficient with OH + COOH was kept for more than 300-s of rubbing. Friction coefficient at the initial stage of the rubbing by the ball-on-reciprocating-flat also indicates better tribological properties of OH + COOH than those of NH + COOH, as expressed in figure 13.

Chemical images of the flat surface after the ball-on-reciprocating-flat test are shown in figures 14–15. The intensity of total positive ions on rubbing track was much higher than those of outside of the rubbing track. Careful analysis of the chemical image revealed that the increase in intensity of total ions due to increase in the fragment ion of m/z 28 which is attributed to the base material, Si. The results can be translated as wear of the LB film. In fact, intensity of m/z 2 on the track is lower than that on outside of the track. Wear of the film can be also confirmed by the quasi-molecular fragment ions as well. A positive fragment ion of m/z 270 was found in TOF-SIMS spectra of NH (not shown here) as $M+1$. A

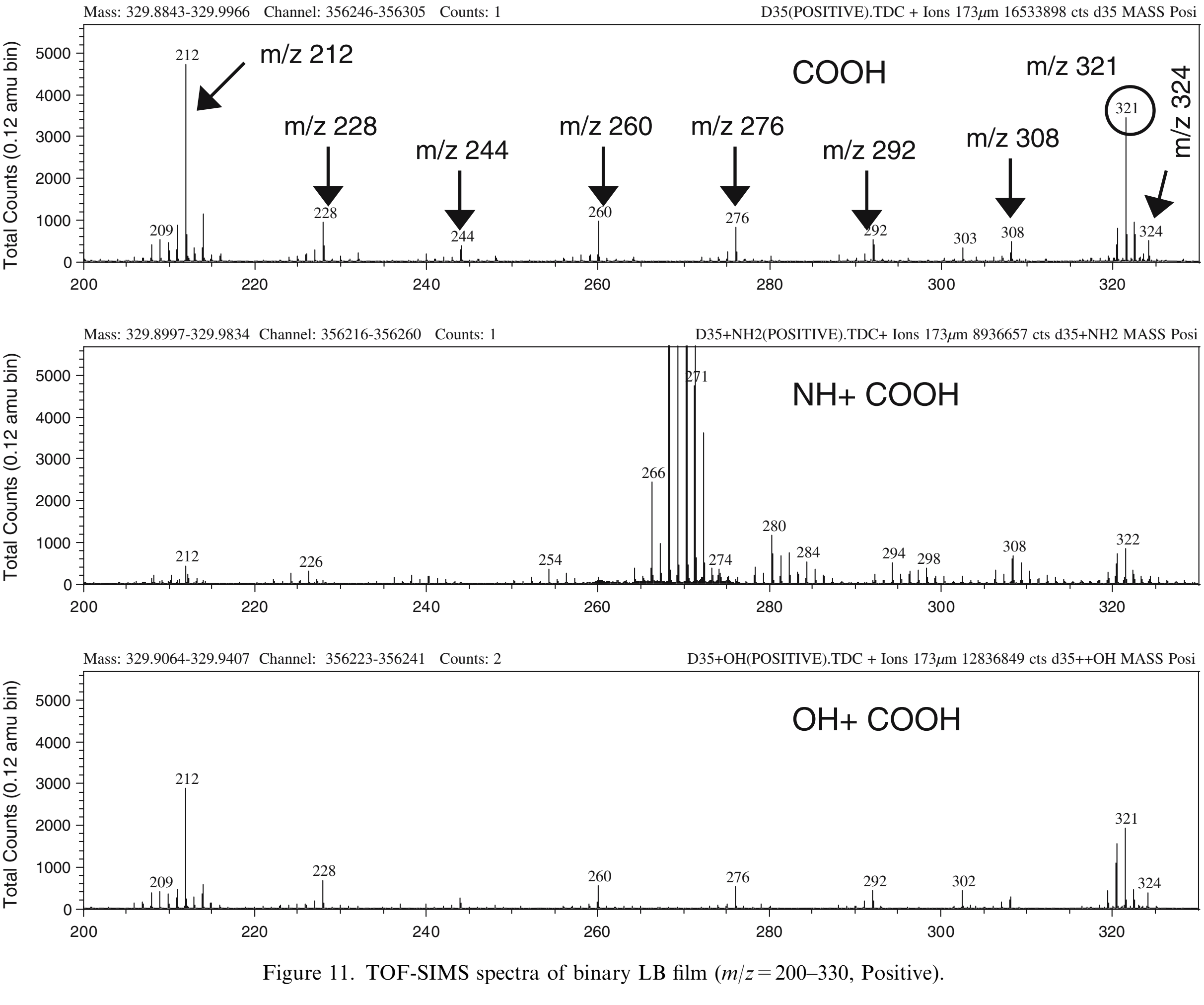

Figure 11. TOF-SIMS spectra of binary LB film (m/z = 200–330, Positive).

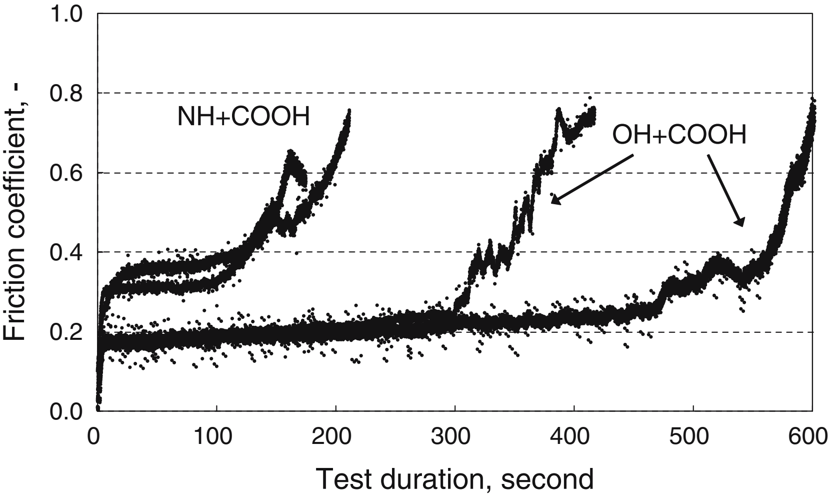

Figure 12. Friction trace during the ball-on-rotating-flat test .

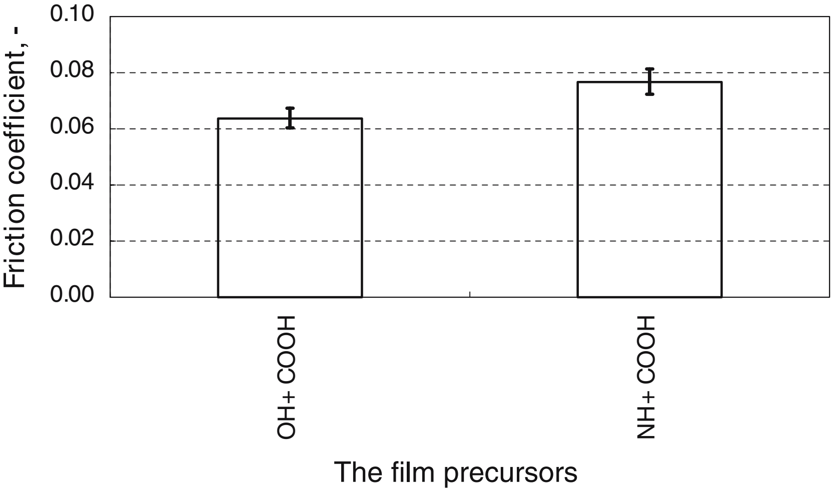

Figure 13. Initial friction coefficient by the ball-on-reciprocating-flat test.

mapping of the fragment ion shows lower intensity on the worn surface than that on outside of the track. The results indicate that NH was removed by rubbing. A mapping of negative fragment ion of *m*/*z* 318, corresponds to $M{-}1$ of COOH, also indicates the removal of COOH from the wear track. Therefore, simultaneous removal of NH and COOH from the wear track under the tribological conditions was found. We considered that the interactions between NH and COOH which mentioned above might result the interaction of the film to the surfaces weaken. Therefore, NH and COOH removed easily by rubbing.

Let us consider the analytical depth of TOF-SIMS and thickness of the LB film. The former has been estimated to be approximately 1 nm [30], and the thickness of monolayer deposited from octadecanoic acid (n-$C_{17}H_{35}COOH$) has been reported as 2 nm [8] to 3 nm [12]. Taking these reports into account, a base material can not be detected by TOF-SIMS analysis if the surfaces were sufficiently covered with monolayer of the acid. Therefore, chemical image of *m*/*z* 28 in Figure 14 indicates clear evidences for removal of the LB film. It should be pointed out that the results show the possibility to detect wear at molecular level or nanometers level if TOF-SIMS analysis was combined with appropriate tracers.

Chemical images of both negative (not shown here) and positive ions did not change at all by the tribo-test if LB film was deposited from OH + COOH after the friction test for 200 s. Although quasi-molecule ion of OH was difficult to detect under the analytical conditions, no changes in the positive fragment ions of *m*/*z* 2, 28 and negative fragment ions of *m*/*z* 318 were confirmed. The results indicate that LB film composed of OH + COOH retained on the surfaces even after the rubbing process. In consequence, the tribological properties of the binary-component LB film are in good accordance with the results of TOF-SIMS analysis.

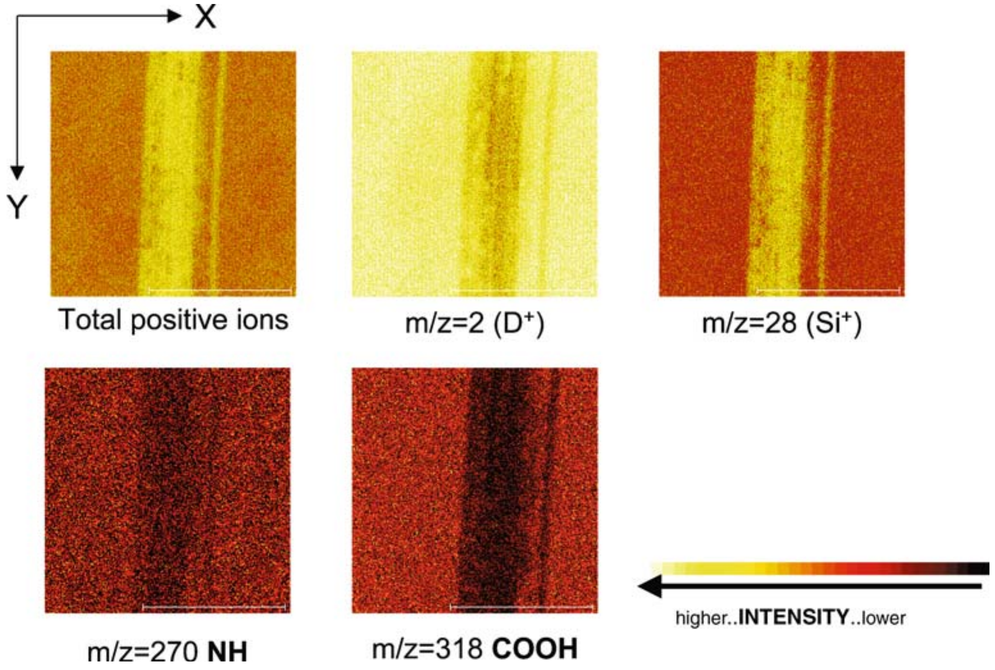

Figure 14. Chemical mapping of NH + COOH after the tribo-test.

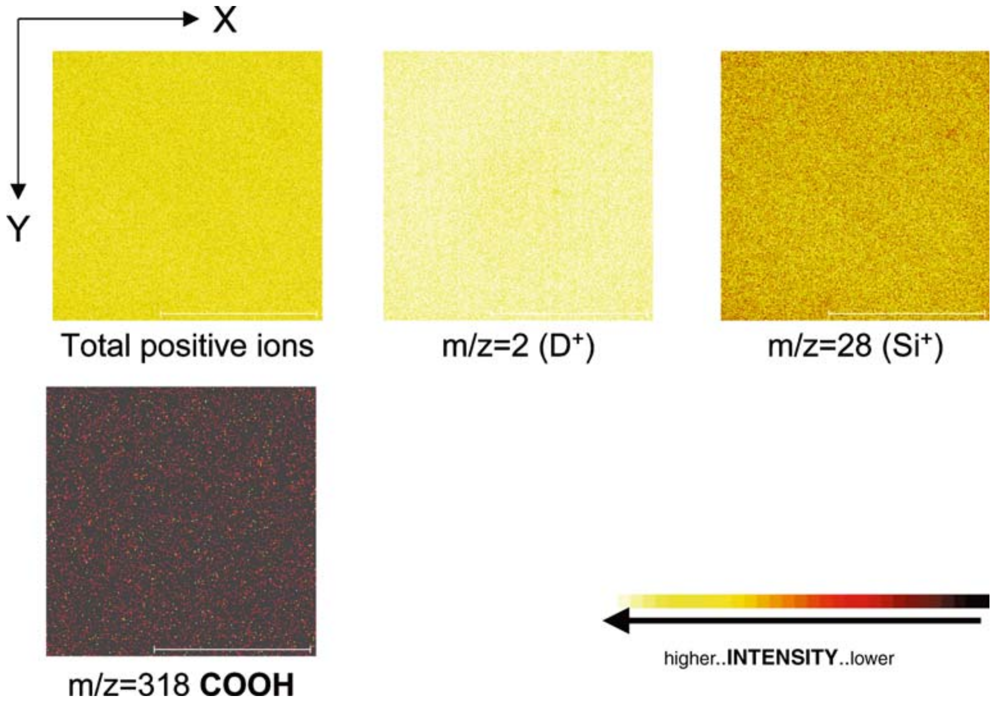

Figure 15. Chemical mapping of OH + COOH after the tribo-test.

4. Conclusions

(1) Perdeuterioalkyl carboxylic acids, in which all protiums in alkyl group were replaced by deuteriums, afford typical fragment ions by TOF-SIMS analysis. Quasi-molecular ions and fragment ion of m/z 2 are noteworthy to trace the molecule during the tribological processes. Particularly, quasi-molecular ion of $M+2$ in a positive spectrum of perdeuterioalkyl carboxylic acids is observed distinctly.

(2) The deuterium-containing fragment ions were detected by the TOF-SIMS analysis of binary-component Langmuir–Blodgett film. Interactions of amines with carboxylic acids were considered by comparing the ratio of positive and negative quasi-molecular ions.

(3) The tribological properties of Langmuir–Blodgett film from octadecanol + octadecanoic acid are superior to those from octadecylamine + the acid. Simultaneous removal of the amine and acid was observed by TOF-SIMS analysis of the rubbed surfaces. On the other hand, the film deposited from octadecanol + octadecanoic acid was retained after the rubbing; thereby provide good tribological properties.

(4) Changes in film structure by rubbing process were analyzed by tracing perdeuterioalkyl group; thereby the role of additives can be understood.

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