Table IV. Energetics of Formation of Methyl Ion from Methyl Chloride and Ground-State Silver and Copper Ions (eV)

	Ag	Cu
$-IP(M)$	-7.576^a	-7.726^f
$-D_{298}°(ClM)$	-3.54^b	$+3.97 \pm 0.05^g$
$+IP(CH_3)$	$+9.81 \pm 0.02^c$	$+9.81 \pm 0.02^c$
$+D_{298}°(ClCH_3)$	$+3.64^d$	$+3.64^d$
$M^+ + CH_3Cl \rightarrow CH_3^+ + MCl$	$+2.33 \pm 0.02$	$+1.75 \pm 0.07$

[a] Reference 11. [b] Reference 17. [c] Reference 21. [d] Reference 19. [f] Reference 12. [g] Reference 20.

$AP(CH_4N^+)$ and $AP(C_3H_8N^+)$ are located between the upper and lower limits specified herein, while for $AP(C_2H_6N^+)$ the extreme upper end of our range overlaps the lower end of their energy spread. Solka and Russell[1] reported a value for $AP(C_2H_6N^+)$ that is midrange to our results. The most recent literature results, reported by Loudon and Webb,[2] give a value for $AP(CH_4N^+)$ that is just at the extreme upper limit of our reported range. However, as can be seen from Table II, they give results about 0.5 eV greater than our upper limit for both $AP(C_2H_6N^+)$ and $AP(C_3H_8N^+)$. Since we had ground-state Ag^+ ions, we can assert that these two values should not be above 10.0 eV.

For proof of ground-state metal ions, we refer back to previous work concerning reactions of methyl halides with Ag^+ and Cu^+.[5] Both of these ions were observed to react with CH_3Cl to give only the simple metal ion–methyl chloride adduct as the initial product (other products were due only to sequential clustering reactions). Tables III and IV give the energetics for the bimolecular fragmentation reactions that are most likely to occur. As can be seen, formation of each of $CuCl^+$, $AgCl^+$, and CH_3^+ is unfavorable for ground-state Cu^+ and Ag^+ ions. If, however, one considers the first excited state, i.e. the $^3D_3$ state, of Cu^+ and Ag^+ (at 10.44 and 12.43 eV,[15] respectively), all four of the reactions become exothermic. For the case of the reaction of Cu^+ ($^3D_3$) with CH_3Cl to form $CuCl^+$ and methyl radical, the exothermicity is 0.07 eV. In fact, Jones and Staley[16] observed $CuCl^+$ as the initial product for this reaction in an ion cyclotron resonance (ICR) cell in which the Cu^+ ions were produced by laser volatilization/ionization of the metal. Since the reaction for ground-state Cu^+ is endothermic, the implication is that excited states of Cu^+ were responsible for their observation of $CuCl^+$ product. In the present work, the $CuCl^+$ product is not observed, and therefore we conclude that excited-state metal ions are absent.

In conclusion, we obtain 9.2 ± 0.2 eV as the lower limit and 9.9 ± 0.1 eV as the upper limit for both $AP(C_2H_6N^+)$ and $AP(C_3H_8N^+)$, while for CH_4N^+ we obtain $9.9 \pm 0.1 \leq AP(CH_4N^+) \leq 10.6 \pm 0.1$ eV.

Acknowledgment. Financial support by the Department of Energy, Grant Nos. DE-AC02-82ER60055 and DE-FGO2-88ER60668, is gratefully acknowledged.

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Quantitative Studies of the Effect of Added Acid and Base on the Sputtering of Organic Amines and Acids from Dilute Glycerol Solution

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Abstract: The addition of strong acids and strong bases to glycerol solutions of organic bases and acids, respectively, has been found to have significant effects on the yield of secondary ions that can be obtained by sputtering. The effects observed are not uniform, however, in that the analyte signal may be either enhanced or degraded by addition of the reagent. Some monofunctional analytes showed enhancement of signal. Polybasic and polyacidic analytes invariably showed strong reductions in secondary ion signal after treatment with acid or base, respectively. The effects observed can be correlated with changes in analyte surface activity (glycerol solubility) that occur when the reagent alters the charge state of the analyte. Drop weight measurements of relative surface tensions have been used to corroborate the trends observed in the SIMS data.

Attempts to improve the secondary ion mass spectrometry (SIMS) sensitivity for organic amines and acids by the addition of mineral acids and bases, respectively, has a long history.[1-4] Such treatments are part of a more general strategy called "reverse-derivatization", which includes all of the various techniques that may be employed to produce a "precharged" form of the analyte.

The general concept of reverse-derivatization as first described by Busch et al.[5] involves the deliberate attachment of polar groups to analyte molecules which initially lack significant polarity. Groups such as quaternary ammonium salts and carboxylic acids have proven especially useful.[4]

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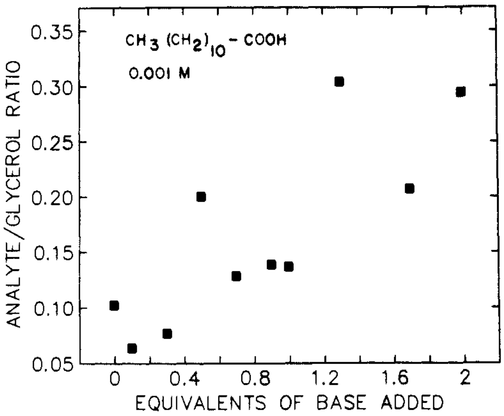

Figure 1. The analyte/glycerol signal ratio obtained in negative ion mode for 0.001 M solutions of lauric acid (I) as a function of increasing concentration of tetramethylammonium hydroxide.

The purpose of reverse-derivatization is to convert the analyte molecule to a form that can be "precharged" before mass spectrometric analysis. The concept arose when it was realized that much improved sensitivities were often obtained for more polar molecules relative to less polar ones. This result was interpreted to imply that materials which already bear a formal charge or can easily become charged are more likely to be charge carriers in chemical ionization-like plasmas of the sort generated by the impact of energetic particles on a surface. In such plasmas, pressures are relatively high. Such high pressures allow many collisions between the various components of the plasma and, accordingly, provide extensive opportunity for charge exchange. These collisions allow the various components of the plasma to approach an equilibrium condition in which those molecules that can most easily stabilize positive or negative charge become the charge carriers. Since only charged species are detected by the mass spectrometer, it is these more stable species that are detected in greatest abundance. Less polar species may provide no signal whatever.

These findings would suggest that in those cases where acid or amine functionality is already present in a molecule, it should be possible to obtain enhanced sensitivity (secondary ion abundance) by merely adding inorganic bases to acids (anion formation) and inorganic acids to amines (cation formation). The success of this strategy has been reported for a number of cases;[2] however, the observations have been qualitative.

During various attempts to employ this technique, we have observed that such additions of acid and base are not uniformly advantageous. In some cases, we have found that sensitivities may actually be substantially reduced. In this paper we will describe experiments that quantify these observations and offer a rationale for the effects observed.

Experimental Section

The SIMS apparatus used for these experiments has been described previously.[6] The primary particle beam was generated from xenon gas and consisted of both ions and neutrals.[7] The effective combined flux of ions and neutrals was about 2 × 10^{12} particles cm^{-2} s^{-1}. The mass spectrometer was adjusted to provide a mass resolution ($m/\Delta m$ 10% valley definition) of 1000 with flat-topped peaks.

Spectra were obtained by magnetic scanning at 256 s per decade and were recorded as an analog signal with a Gould ES1000 electrostatic recorder. Ion current values were obtained by manual measurement of peak heights. All spectra were recorded in triplicate and the measured ion currents averaged to obtain the values reported. Because of the difficulties inherent in reproducing absolute ion current values, all of the results are reported as a ratio to the matrix signal (m/z 93 positive ion mode, m/z 91 negative ion mode).

Drop weight measurements were carried out at room temperature in the laboratory atmosphere with use of a disposable pipet as a reservoir with collection of the droplets on the pan of a conventional electronic balance. About 100 drops were collected for each drop weight determination.

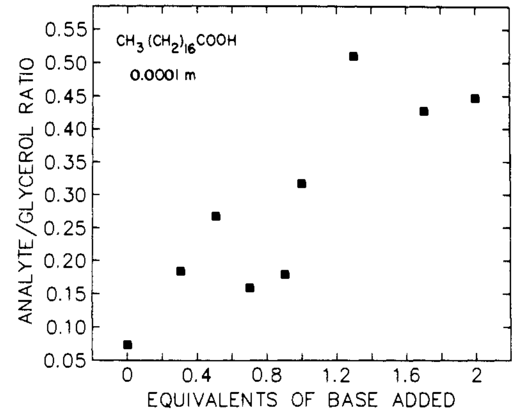

Figure 2. The analyte/glycerol signal ratio obtained in negative ion mode for 0.0001 M solutions of stearic acid (II) as a function of increasing concentration of tetramethylammonium hydroxide.

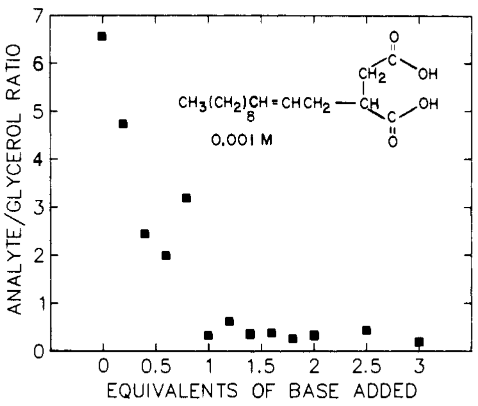

Figure 3. The analyte/glycerol signal ratio obtained in negative ion mode for 0.001 M solutions of dodecenylsuccinic acid (III) as a function of increasing concentration of tetramethylammonium hydroxide.

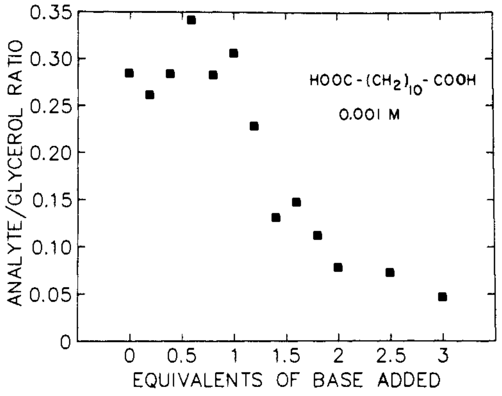

Figure 4. The analyte/glycerol signal ratio obtained in negative ion mode for 0.001 M solutions of 1,10-dodecanedicarboxylic acid (IV) as a function of increasing concentration of tetramethylammonium hydroxide.

All solutions examined were prepared in glycerol. For each individual solution the analyte and the appropriate quantity of acid or base were first combined in a small vial and thoroughly dried in a stream of filtered nitrogen gas before addition of the glycerol solvent. This procedure ensured that the samples were free of water, both from the reagents and from the water of neutralization. In some cases, small amounts of a volatile co-solvent such as methanol wered utilized to facilitate the dissolution of the samples in glycerol. Solutions for drop weight studies were always prepared without the use of volatile co-solvents because such solvents cannot be easily removed completely from glycerol and therefore can serve to obscure differences in surface tension.

The sources of the compounds studied were as follows: Lauric acid (I), stearic acid (II), 2-dodecen-1-ylsuccinic acid (III), 1,10-decanedicarboxylic acid (IV), and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclo-

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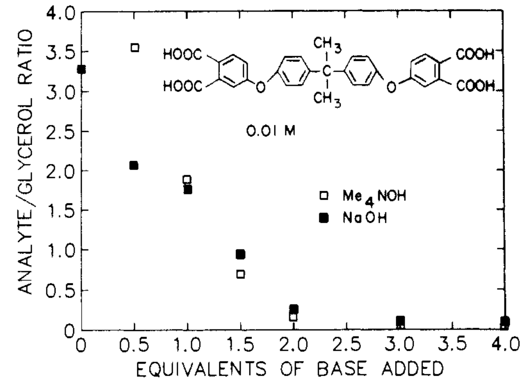

Figure 5. The analyte/glycerol signal ratio obtained in negative ion mode for 0.01 M solutions of the tetraacid V as a function of increasing concentration of tetramethylammonium hydroxide and independently sodium hydroxide.

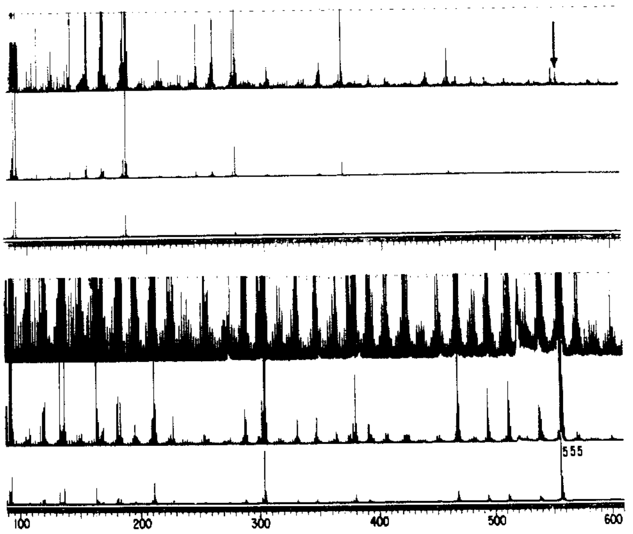

Figure 6. A comparison of the full negative secondary ion mass spectra obtained for a 0.01 M solution of V before (bottom) and after (top) addition of 2 equiv of tetramethylammonium hydroxide. In the top spectrum the signal obtained for the molecular anion at *m*/*z* 555 is indicated with an arrow. The major ions appearing in the top spectrum correspond to glycerol and its clusters. It should be emphasized that these two spectra were obtained sequentially with identical instrument conditions.

tetradecane (VII) were obtained from Aldrich Chemical Co., Milwaukee, WI. *N*,*N*,*N*-Tris(3,6-dioxo-*n*-heptyl)amine (VI) was obtained from Rhone-Poulenc Specialites Chimiques, 19 Boucle d'Alsace, Courbevoie, France. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane (V) was obtained synthetically by the method described in ref 8.

Unless otherwise noted tetramethylammonium hydroxide was used as the strong base and hydrochloric acid was used as the strong acid.

Results and Discussion

We report the effect of added base on the response obtained for two monocarboxylic acids (lauric acid (Figure 1) and stearic acid (Figure 2)), two dicarboxylic acids (2-dodecen-1-ylsuccinic acid (Figure 3) and 1,10-decanedicarboxylic acid (Figure 4)), and one tetracarboxylic acid (V (Figure 5)). In addition, we report the effect of added acid on the response obtained for one monoamine (VI (Figure 7)) and one tetraamine (VII (Figure 8)).

Organic Carboxylic Acids. For studies of carboxylic acids, the mass spectrometer was adjusted to analyze negatively charged secondary ions. In every case, the analyte species observed was the mono-anion of the respective carboxylic acid.

As may be seen in the figures, the signal for both monocarboxylic acids is enhanced by the addition of base. In each case, the relative signal improves by approximately a factor of 10. It should be noted that this does not reflect an increase of 10 in the absolute signal for the analyte but rather reflects the combined effect of reduced glycerol signal and increased analyte signal. For monocarboxylic acids, most of the change in ratio is caused by reduction of matrix signal. It is of interest that the ratio continues to increase beyond 1 equiv of base. Although not shown in Figure 1, we have added large excesses of base to similar lauric acid solutions and found that the ratio continues to increase slowly as base is added, eventually reaching a value of about 0.7 at 10 equiv. This effect is not fully understood but may reflect a phenomenon that surface chemistry texts call "surface hydrolysis"[9] in which cations (e.g., tetramethylammonium, sodium) at a surface are replaced by hydrogen ions generating the neutral carboxylic acid. An alternative formulation of this idea, perhaps more familar to most chemists, would suggest that a small but finite amount of acid always exists in equilibrium with the carboxylate salt and since this acid is intrinsically less soluble it will tend to populate the near-surface region. Continuing to increase the base present in the bulk, as in the experiment described, would be expected to reduce the equilibrium amount of free acid and, conversely, to increase the fractional contribution of carboxylate salt to the surface. This relatively slow shifting of an equilibrium offers a plausible rationale for the observed continuing increase in analyte/glycerol ratio in response to additions of strong base far exceeding the 1 equiv required for neutralization.

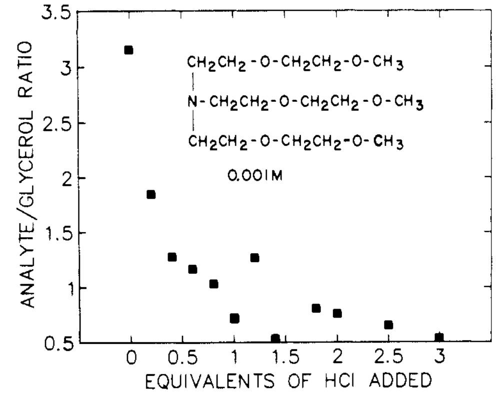

Figure 7. The analyte/glycerol signal ratio obtained in positive ion mode for 0.001 M solutions of the monoamine VI as a function of increasing concentration of hydrochloric acid.

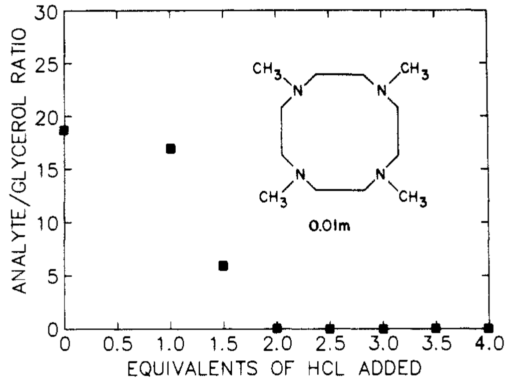

Figure 8. The analyte/glycerol signal ratio obtained in positive ion mode for 0.01 M solutions of the tetraamine VII as a function increasing concentration of hydrochloric acid.

As will be demonstrated later by an independent method (see Drop Weight Measurements), the addition of base results in a net reduction in the amount of analyte at the surface, presumably because formation of a carboxylate salt increases glycerol solubility. The ionization of the analyte and its resulting migration away from the near-surface region have exactly opposite effects

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on the intensity of the signal observed. For simple monocarboxylic acids, we have observed a net increase in signal. For these substances, therefore, we are led to conclude that the increase in ion abundance brought on by "precharging" more than compensates for the loss of analyte from the surface. Solubility effects are, however, strong functions of molecular structure and it is reasonable to expect that the gain in signal from precharging may not always compensate for the loss in signal incurred because a fraction of the analyte migrates away from the surface. Other substances that lack the classical surfactant-like structure of long-chain monocarboxylic acids may behave quite differently.

In Figures 3 and 4, we see that addition of base to a dicarboxylic acid may actually reduce the signal obtained. The signal for III is largely degraded by only 1 equiv of base. The signal for IV is unchanged by 1 equiv of base then gradually degrades until about 3 equiv of base have been added. As suggested above, *the net effect of introducing charge is highly dependent on molecular structure*. To rationalize this result, we need only to propose that ionized diacids have such high polarity (and high glycerol solubility) that they *effectively lose their surface activity*. [Note that for purposes of this discussion, "surface activity" is meant to refer to that property of a solute expressed in a given solvent which produces a "surface excess"[10] (or surface deficiency) of solute, in an arbitrarily defined near-surface region, relative to the bulk concentration of the solute. This modified near-surface composition is defined in terms of activity coefficients by the Gibbs equation.[10]] If sample molecules have migrated out of the near-surface region, and therefore are not accessible to the primary beam, they cannot appear in the SIMS spectrum.

It has been argued that it is energetically unfavorable to sputter multiply charged ions in the SIMS experiment.[11] On this basis, one might suggest that the diacid samples have not been removed from the surface as described above, but rather have simply been converted to a form that cannot be sputtered. While it is true that doubly charged ions are almost never observed with a glycerol matrix (but may be observed with other matrices[12]), it happens that the spectra generally do provide evidence of the presence of a multiply charged species when such species exist at the surface. That evidence takes the form of cluster ions of the type (M--X+)- or (M+ +X-)+, which have a net charge of one and therefore behave like singly charged ions. We have searched all of our spectra for evidence of such cluster ions without success and therefore take their absence as further confirmation that the sample is being removed from the surface.

In Figure 5, we find that for the tetraacid V, the addition of 1 equiv of base has little effect, but 2 equiv results in a 20-fold reduction in signal. The figure provides results for the use of two different bases; tetramethylammonium hydroxide and sodium hydroxide. It may be noted that the result is independent of the nature of the base employed. Cluster ions are not observed in the spectra. Using a rationale similar to that provided above for the behavior of diacids, we would propose that this tetraacid loses all surface activity after addition of 2 equiv of base and under these conditions is actually excluded from the near-surface region. Addition of base beyond 2 equiv does not result in significant further reduction in signal. This is consistent with the idea that it is surface chemistry and not charge state that is the major controlling influence on the abundance of ions observed. Even though the molecule is converted to a triply and ultimately quadruply charged form, the abundance of singly charged ions observed in the SIMS spectrum does not fall significantly. This clearly suggests that the solution charge state is of relatively minor importance in controlling sensitivity. It would appear that the energy of the plasma created by primary particle impact is sufficient to allow a redistribution of charge which ultimately produces singly charged ions independent of the original charge state of the analyte.

Figure 6 provides a comparison of the full SIMS spectrum obtained for a 0.01 M solution of V without base addition, and the same solution after addition of 2 equiv of base.

Amines. For studies of amines the mass spectrometer was adjusted to analyze positively charged secondary ions. In each case the species observed was the singly charged cation formed from the respective amine.

Figure 7 reports the results of our studies of a tertiary monoamine. In contrast to the case of a monoacid, treatment of monoamine VI with acid causes a reduction in the analyte signal relative to the matrix signal. This result may simply imply that for this relatively polar amine, a single charge center is sufficient to cause the material to become exceedingly soluble in glycerol and therefore to lose its surface activity. As suggested earlier, the effect of introducing a charge center into an analyte on its glycerol solubility is a strong function of molecular structure. Accordingly, attempts to predict in advance the effect of forming a charge center will be limited by our ability to predict changes in glycerol solubility with charge.

The result of adding acid to a glycerol solution of a tetraamine is shown in Figure 8. In this case the result is very similar to that obtained for a tetraacid. One equivalent of acid has little effect on response, but the signal is rapidly degraded when 2 equiv of acid are added. Addition of acid beyond 2 equiv has no further effect on the ratio. The loss in analyte signal between 1 and 2 equiv of acid is especially large, however, amounting to a factor of about 170.

Taken together, these results suggest that the surface chemistry based rationale proposed to explain our negative ion carboxylic acid data can be extended to experiments involving positive ion data obtained on amines.

It is important to note that for the cases of both acid and amine analytes, the changes in SIMS response observed for addition of base and acid reagents are very likely to exhibit an additional strong dependence on bulk concentration of the analyte—an effect that we have not attempted to demonstrate here. By this we mean that although the trends should be the same, the functional dependence presented in Figures 1–5, 7, and 8 will most likely not be reproduced exactly at different bulk concentrations of analyte. This additional dependency arises from the interplay of solubility limits or in certain cases "critical micelle concentrations" and has been discussed in detail previously.[6]

The reader must also be aware that the results reported here are sensitive to the intensity of the primary particle flux. Very high flux values are capable of eroding the surface faster than analyte-enhanced surface compositions can be re-established. Accordingly, very high fluxes produce SIMS spectra that are characteristic of the bulk of the solution. This dependence has been described in detail elsewhere.[6]

Drop Weight Experiments. Changes in surface composition such as those postulated to occur in the experiments described above are known to result in changes in surface tension.[10] A classical method for obtaining relative surface tension measurements involves the simple determination of drop weights. Higher drop weights are related to higher surface tensions (γ) according to the following relationship[13]

$$W = 2\pi r\gamma f$$

The variables and constants are defined as follows: W, drop weight; r, drop radius; f, correction factor. The correction factor can be large and is determined from solution density and the uncorrected drop weight. For very similar dilute solutions, solution density is very nearly constant and therefore for small changes in drop weight the correction factor f is nearly constant. Under such conditions the drop weight should depend only on the surface tension and the correction factor can be neglected if only relative measurements are desired. Because of its simplicity, we decided to use this simple drop weight method to determine if our proposed

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(10) Adamson, A. W. *Physical Chemistry of Surfaces*; Interscience Publishers, Inc.: New York, 1960; p 75.

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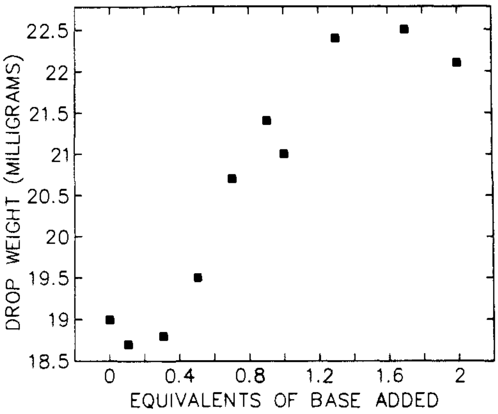

Figure 9. The variation in drop weight for 0.001 M solutions of lauric acid (I) as a function of increasing concentration of tetramethylammonium hydroxide.

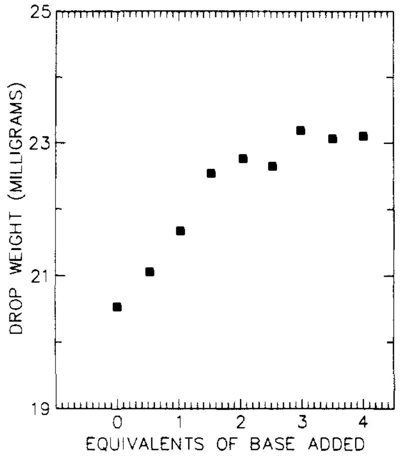

Figure 10. The variation in drop weight for 0.01 M solutions of the tetraacid V as a function of increasing concentration of tetramethylammonium hydroxide.

changes in surface composition could be correlated with changes in surface tension.

Utilizing exactly the same solutions that were employed to obtain the respective SIMS spectra, we have examined the change in surface tension which occurs when base is added to lauric acid (Figure 9) and to the tetraacid V (Figure 10). For these solutions the measured density was constant within the accuracy of the measurement (0.005) *g* and had a value of about 1.260 g/mL, and therefore within the range of drop weights found, the correction factor was very nearly constant at about 0.62.[13] Because the correction factor was very nearly constant, it has not been applied to the drop weight data shown in the figures. The drop weight of a sample of the pure glycerol used for preparing these solutions was 0.0257 g.

In both cases it may be noted that addition of base causes an increase in drop weight which implies that hydrocarbon-like species are being removed from the surface and replaced with glycerol. This explanation is in good agreement with a rationale which suggests that precharging of an analyte increases glycerol solubility, causing a decrease in the near-surface concentration of the analyte. This effect serves to diminish the number of molecules available to the sputtering process. However, as noted earlier, for the case of lauric acid, the effect of precharging brought on by the addition of base appears to more than compensate for the net migration of analyte (charged and uncharged) away from the near-surface region which is confirmed by the drop weight data.

Practical Implications. These results would appear to suggest that an analyst who is faced with limited quantities of a difficult and valuable sample would be well advised to avoid the use of acid and base treatments. Improvements, when obtained, are likely to be small even in the best cases. In the worst case, losses in sensitivity may cause the analysis to fail. Our ability to predict in advance the likelihood of success is no better than our ability to predict glycerol solubilities.

As alternatives, the analyst can consider the use of acid and base reagents that are themselves surface active.[14] Long-chain quaternary ammonium hydroxides are strong bases and long-chain sulfonic acids are relatively strong acids. Because of their inherent surface activities, these materials segregate to the surface. In short, the glycerol solubilities of these reagents are relatively predictable.

When an analyte molecule is protonated by a long-chain sulfonic acid, this creates an ion pair that tends to remain associated and near the surface. Likewise, when an analyte is deprotonated by a long-chain alkylammonium hydroxide, an ion pair is created that tends to remain near the surface. This effect allows the analyst to obtain the advantages of a preformed ion while minimizing the likelihood that the analyte will be completely removed from the surface. However, each individual ion pair behaves as a new chemical species and has its own unique solubility determined by both the analyte and the reagent. As a result, surface active reagents cannot be expected to provide exactly the same enhancement for every sample.

An additional complication with polyamines and polyacids is that the use of surface active reagents frequently leads to formation of clusters of the type (M+ +X−)+ or (M− −X+)−, where X is the surface active reagent. The polyacid V when treated with tetradecyltrimethylammonium hydroxide produces *exclusively* the (M− −X+)− ion at all concentrations of reagent from 0.1 to 4 equiv. Other materials such as adenosine triphosphate produce only (M−) ions after treatment with similar reagents.[15] At present we have not been able to develop a rtionale that will allow a prediction of which materials will tend to form clusters and which will not.

Conclusion

The concept of reverse-derivitization as originally formulated for solid-state SIMS samples[5] should not be applied uncritically to experiments involving a liquid matrix. While it remains quite clear that for highest sensitivity an analyte molecule must be able to readily accept charge subsequent to primary particle impact, our results suggest that for liquid matrices the beneficial effects on sensitivity obtained by introducing an ionic functionality into an analyte molecule may be offset to varying degrees by losses in surface activity. Accordingly, a modification of the reverse-derivitization concept more relevant to solutions might reasonably suggest that for greatest sensitivity, the chemical modifications employed should introduce readily ionized functionality into an analyte while avoiding the introduction of truly ionic functionality. Even this concept must be carefully applied, since our ability to predict the effect of a given chemical modification on SIMS sensitivity is no better than our ability to quantitatively predict changes in glycerol solubility caused by that modification. Such predictions are notably imperfect and can constitute at best rough guidelines.

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(14) Ligon, W. V.; Dorn, S. B. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *61*, 113.

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