Characterization of Some Liquid Phases for Fast Atom Bombardment Mass Spectrometry

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Introduction

Fast atom bombardment (FAB) mass spectrometry is a desorption ionization technique which requires sample dissolution in a liquid matrix (1). The matrix acts as a sample reservoir, providing a continual replenishment of sample to the surface under bombardment. It acts further as an energy buffer which lessens the severity and extent of irradiation damage by the energetic primary atom beam. Liquid matrices commonly used in FAB share similar physical properties of chemical inertness, vacuum compatibility, and a non-interfering background mass spectrum. However, these matrices differ considerably in their chemical properties, and in their more specific physical properties. A number of liquid matrices have been employed in the analysis of different compound classes (2), each found to be "optimum" for that particular problem.

Our work over the last few years has categorized the various solution processes which affect ion abundances in FAB mass spectra (Figure 1). The direct desorption
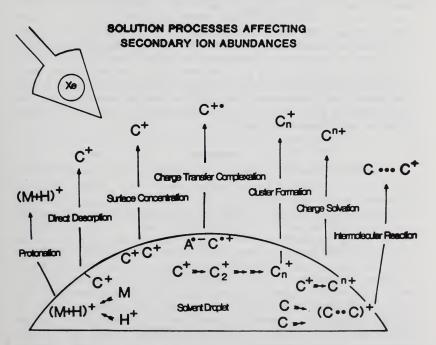

FIGURE 1. Summary of the solution processes which affect the nature and abundances of the ions observed in a FAB mass spectrum.

process is very efficient, reflecting the ease with which preformed ions can be liberated from the solvent into the gas phase. Concentration of the sample molecules and ions at the surface (surfactancy) also increases the abundances of the corresponding ions

in the FAB mass spectrum. Processes of protonation and charge transfer complexation both create preformed ions in the solvent matrix which can then be sputtered directly into the gas phase. The abundance of multiply-charged ions in the mass spectrum is thought to reflect the charge solvation properties of the solvent. The measured extent of cluster formation evaluates a similar property, viz, the extent of intermolecular cluster formation in the solvent. Some of the ions observed in FAB mass spectra are the result of intromolecular reactions, and these processes must also be measured, using as test compounds molecules which are predisposed to so react.

A characterization of FAB matrices is presented in which the mass spectra of a series of standard compounds, representing the processes described above, are quantitatively compared as the solvent is varied. The data generated can be used in an informed choice of FAB solvent, rather than an empirical or intuitive selection as has been practiced to date. The correct choice of solvent is critical when only small amounts of sample are available. For purposes of mechanistic study, the quantitative evaluation of the standards and their behavior in the various FAB matrices stands on its own merits.

Experimental

Compounds used in the study were obtained from commercial sources and used without further purification. Sample concentrations in the FAB solvents were 2-10 micrograms per microliter, with a 5 microliter aliquot loaded onto the FAB probe. Mass spectra were obtained on a Kratos MS80RFAQQ hybrid geometry mass spectrometer, using the intermediate detector, an accelerating potential of 4 keV, a resolution of 1,000, and a magnet scan speed of 10 s/decade. The FAB source was an IonTech saddle field gun, using xenon as the source of gas, an accelerating potential of 7 keV, and a regulated ion current in the gun of 30 microamps. A rigorously uniform sample introduction method is necessary for the reported reproducibility. Data is collected three minutes after introduction of the sample into the high vacuum of the source. Solvent degassing during the first few minutes of exposure to vacuum is a major contributor to sample-to-sample variability.

Discussion

A quantitative description of FAB solvents requires representative standards for specific solution processes, a uniform analysis protocol, and a uniform method for data reduction. The most difficult of these three requirements to meet is the selection of a satisfactory group of spectral standards. Our preliminary set of seven standards were tetraphenylphosphonium bromide (direct desorption), cetyltrimethylammonium bromide (surface concentration), methyl red (protonation), the complex between hexanitrosobenzene and napthalene (charge transfer complexation), hemicholinium-3-hydrate (charge solvation), cesiumtrifluorobutanesulfonate (cluster formation), and carnitine hydrochloride (intermolecular reaction). Selection was based on several criteria, foremost among which was the assumption that each standard independently represents the solution process indicated. Each standard had been previously analyzed by FAB or the closely related secondary ion mass spectrometry, and the mass spectrum of each contains an abundant ion that could be used for quantitation. All were readily available in high purity at reasonable cost.

The absolute signal intensity, given as counts per microgram, for the characteristic ions is obtained from the mean value obtained from several scans. For example, measurement of the intensity of the intact cation 339+ of tetraphenylphosphonium bromide (TTPB) averages the signal for scans 4-8 inclusive. Figure 2 demonstrates the constancy of the absolute response value measured for TPPB over several scans for both
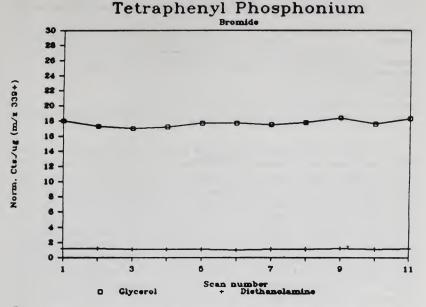
FIGURE 2. Reproducibility of the signal from the intact cation of tetraphenylphosphonium bromide in the solvents glycerol and diethanolamine.

glycerol and diethanolamine. The figure also reflects the greater response obtained for this ion sputtered from glycerol as compared to diethanolamine. Data for this analysis repeated over several days is presented in Table 1. Reproducibility is within 10% for diethanolamine, and within 2% for glycerol. We feel that the difference in these values is due to the fact that our sample introduction method is optimized for glycerol. These values are attainable without the use of an internal standard, which from first principles might compromise the independence of the response values obtained.

TABLE 1. Reproducibility of absolute response values for the intact cation of tetraphenylphosphonium bromide sputtered from glycerol and diethanolamine.

Sample	Amount (ug)	Counts	Counts per ug
GLYCEROL			
1	10.0	110,312	11,031
2	9.0	103,412	11,120
3	9.0	106,040	10,820
4	8.2	86,692	10,572
5	15.5	167,844	10,829
			n = mean = 10,874 +/− 213 (2%)
DIETHANOLAMINE			
1	7.8	4169	535
2	13.8	7995	579
3	11.4	7194	631
4	11.4	7640	670
			n = 4, mean = 604 +/− 59 (10%)

TABLE 2.   Relative sensitivities for standard compounds in glycerol and diethanolamine.

Compound	Glycerol	Diethanolamine
Tetraphenylphosphonium bromide	350	20
Cetyltrimethylammonium bromide	1000	960
Methyl Red $(M+H)^+$	5	3
Hemicholinium-3-hydrate $(M^{2+}$	0.5	1
Carnitine hydrochloride (M^+)	5	4

The relative response values for all of the standards studied are summarized in Table 2 for glycerol and diethanolamine. The values given are normalized to the largest response obtained, that is, that for the surfactant standard in glycerol solvent; this is arbitrarily set to a value of 1000. The data in the table clearly reveal the ease with which surface-active molecules and performed ions are sputtered from the matrix. A surprising difference in the efficiency of direct desorption from the two solvents was noted, as this is generally conceded to be a solvent-independent process. Surfactancy may account for the observed difference in the response values. Interestingly, protonation of the methyl red molecule was observed in both the acidic and the basic solvents with near equal facility. Accordingly, another standard to represent the acidity of the solvent is being evaluated. Diethanolamine is indicated to be the preferred solvent for the analysis of multiply-charged ions, but this conclusion will have to be studied with additional standards before it can be generally verified.

Conclusions

The quantiative evaluation of FAB solvents for the analysis of a series of standard compounds is evaluated for the first time. A large data base which documents the behavior of an expanded group of standards in a number of the other commonly used FAB solvents is necessary before the response values measured can become generally useful. The reproducibility of the measurements is sufficient for the creation of this data, provided careful attention is given to the mechanics of sample introduction.

Acknowledgments

Literature Cited

1.   Barber, M., Bordoli, R. S., Elliot, G. J., Sedgwick, R.D., Tyler, A. N. 1982. Fast Atom Bombardment Mass Spectrometry. Anal. Chem., *54*(4): 645A-657A.
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