Fundamentals and Applications of Electrospray Ionization Mass Spectrometry for Petroleum Characterization

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We are reporting a study of the fundamental and application aspects of positive-ion electrospray ionization (ESI+) for petroleum characterization. In the positive-ion mode, basic nitrogen molecules (typically pyridinic molecules) form predominantly protonated molecule ions. Most other molecular types, such as paraffins, naphthenes, aromatics, and thiophenoaromatics, are largely not ionized by ESI. Metalloporphyrins and neutral nitrogens show little response. The effects of acid and analyte concentrations, and instrumental conditions, were evaluated. Increasing the acid concentration promotes the ionization of the low-molecular-weight bases but has minimal impact on high-molecular-weight species. Analyses of low- and high-molecular-weight petroleum fractions and their mixtures showed minimal mass discrimination. Cone and extraction voltages have a significant impact on ESI responses, particularly on aliphatic amines. Linear dynamic range exists at lower analyte concentrations ($<10^{-5}$ M).

Introduction

Since its reintroduction in the mid 1980s by Fenn et al.,[1] electrospray ionization mass spectrometry (ESI−MS) has rapidly found a wide range of applications in the analysis of both large- and small-molecule systems.[2−6] Currently, ESI−MS has become an indispensable analytical tool in proteomic and pharmaceutical research. Its applications for petroleum characterization came more than a decade late, partially because ESI is traditionally considered a technique that is most suitable for molecules that have polar functionalities and petroleum is known to be largely composed of hydrocarbon molecules. Zhan and Fenn first attempted to apply ESI to a range of petroleum products, including gasolines, jet fuels, diesels, and crude oils.[7] Although their quadrupole mass spectrometer applied in the study did not have sufficient mass resolution to separate isobaric molecules and determine their composition, it clearly demonstrated that petroleum products contain many polar molecules that can be ionized by ESI. More in-depth studies came from collaborative research be-

tween the National High Magnetic Field Lab at Florida State University and ExxonMobil Research and Engineering Company (Annandale, NJ) on high-field Fourier transform ion cyclotron resonance (FTICR) applications to petroleum characterization. A large number of polar compounds in a crude oil were detected, yielding the most-complex mass spectrum ever recorded at the time (∼7 components per nominal mass).[8] High-field FTICR showed its unmatched power in determining elemental compositions of >3000 mass peaks in a single analysis and was applied to characterize metalloporphyrins and basic and acidic species in heavy crude oils under positive- and negative-ion conditions.[9−12] On-line liquid chromatography−electrospray ionization tandem mass spectrometry (LC−ESI−MS) was recently used to determine polycyclic aromatic hydrocarbons (PAHs), mostly 3- to 5-ring condensed aromatics in water.[13,14] Nonpolar petroleum molecules were shown to be ionizable when co-sprayed with Pd and Ag salts.[13−16]

The high selectivity of ESI added a significant advantage to the analysis of trace polar compounds in

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petroleum. However, it also introduced complications in quantitative analysis of composition of petroleum products, where the size, structure, and composition of analyte molecules vary significantly. For practical applications, one must understand what petroleum molecules can be ionized by ESI and what are the critical molecular properties that determine the ionizability (or ionization efficiency) of petroleum molecules.

The fundamental mechanisms of the ESI process have been the subject of research over the past decade. However, the exact mechanisms are still under scrutiny.[17−23] For analytical chemists, it is most important to understand how the ESI process affects the MS response. Kebarle and co-workers first proposed a model to predict matrix and analyte effects on ESI sensitivities for ionic analyte systems.[18,24,25] Enke further advanced the model, based on the concept of excess charge equilibrium between the inner layers and the surface.[26] The model provided an excellent fit of ion intensity curve over a full concentration range for single and multi analyte systems.[26] However, the development of a fundamental model for ESI remains a challenge,[22,27,28] and there are continued efforts to understand the factors that affect ESI response for both practical and fundamental reasons.[19,29−32]

Petroleum is a special class of chemicals that contains mostly nonpolar hydrocarbons. Even the most-polar species in petroleum, such as basic nitrogen and naphthenic acid molecules, are considered to be weak bases and weak acids. Therefore, the behaviors of petroleum polar molecules in ESI are different from that of the ionic analytes. The focus of this work is to understand the impact of experimental conditions and molecular properties on the ionization of petroleum molecules, which are critical to the application of ESI for petroleum characterization.

Experimental Section

Samples and Preparation. All model compounds were purchased from Aldrich and used as-is. Petroleum samples (0.5−1 g) were normally first dissolved in 10 mL of toluene. One milliliter of the toluene solution was then diluted with 19 mL of acetonitrile. Twenty microliters of acetic acid (99.9%)

was added to promote ionization. Petroleum distillates were obtained from ExxonMobil Research & Engineering Company in Annandale, NJ. The polar fractions of the naphtha sample and petroleum distillates were obtained using a clay−gel separation procedure that was similar to that described in ASTM Standard D 2007, where petroleum products are fractionated into the hydrocarbon types of polar compounds, aromatics, and saturates.

Instrumental Conditions. All ESI experiments were conducted on a MicroMass Quattro II mass spectrometer with a Z-spray ESI source. Samples were introduced using a syringe pump with a flow rate of 10 μL/min. For most of our experiments, the source temperature was set at 120 °C and the probe temperature was set at 200 °C. The drying gas flow was 300 L/h. Cone and extraction voltages were set at 30 and 10 V, respectively. The mass range was set at 50−800 Da, with a scan speed of 3 s/scan.

Gas chromatography/mass spectroscopy (GC/MS) analysis of naphtha polars was conducted on a VG-70 mass spectrometer coupled with a Hewlett Packard model HP-5890 gas chromatograph, using a 30-m-long DB-1 column (0.25 mm inner diameter (ID), 0.25 μm film thickness). The GC oven temperature was programmed from 40 °C to 300 °C at a rate of 10 °C/min. The mass range is set at 33−600 Da, with a scan speed of 1 s/scan. The GC effluents were ionized under 70 eV electron impact (EI) ionization conditions.

Discussion

Electrospray Ionization of Petroleum Model Compounds. In ESI, a large potential of ∼2000−4000 V is applied to a capillary needle through which a sample solution containing an electrolyte (e.g., acetic acid for positive ions) is introduced. A counterelectrode is maintained at 0 V, thus creating a strong electric field between it and the capillary. The electric field permeates the solution at the tip of the capillary needle and causes separation of the ions in solution. The repulsion of the excess charges at the surface and the pull of the electric field form a "Taylor cone" at the tip of the capillary. As the charge repulsion overcomes the surface tension of the liquid, a fine spray of charged droplets is created. Coulombic repulsion causes droplets to fission into successively smaller daughter droplets, resulting in the eventual removal of all solvent molecules to yield unhydrated gas-phase ions (charge residual model) or the direct ejection of ions into the gas phase (ion evaporation model).

Petroleum is a very complex mixture of hydrocarbon molecules, containing paraffins, cycloparaffins (naphthenes), and aromatics. Virgin crude oils can contain molecules with a wide boiling range, from gaseous hydrocarbons to nonvolatile asphaltenes. Some of them contain heteroatoms (most commonly N, S, O) and metals (most commonly V and Ni in the form of metalloporphyrins). The polar molecules in petroleum are typically nitrogen-containing compounds, acids, and metalloporphyrins. Figure 1 illustrates the classes of molecules that are commonly found in petroleum. The high selectivity of ESI for polar molecules, with respect to nonpolar molecules, is shown in Table 1, which lists the relative responses of equal moles of nine typical petroleum molecules. Saturate hydrocarbon types (dodecane and decyl cycloparaffin) showed essentially no response in ESI. Aromatics and some heteroatomic aromatics (naphthalene, phenanthrene, dibenzothiophene, and carbazole) yield very low responses.

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Table 1. Electrospray Ionization Selectivities of Petroleum Molecules

compound	ions	gas-phase basicity, GB (kcal/mol)	molecular weight, MW	relative response
acridine	$M + H^+$	224.8	179	28.66
aniline	$M + H^+$	203.3	93	1.39
carbazole	$M + H^+$		167	0.08
dodecane	$M + H^+$		170	0.00
decyl cyclohexane	$M + H^+$		224	0.00
naphthalene	$M + H^+$	186.3	128	0.01
phenanthrene	$M + H^+$	190.0	178	0.06
dibenzothiophene	$M + H^+$		184	0.01
vanadyl octaethyl porphyrin	$M + H^+/Na^+$		599	2.07

A relative higher response was observed for aniline and vanadyl porphyrin. The latter also forms a sodiated molecular ion, in addition to the protonated ion. Acridine, which is the most basic compound, dominates the spectrum.
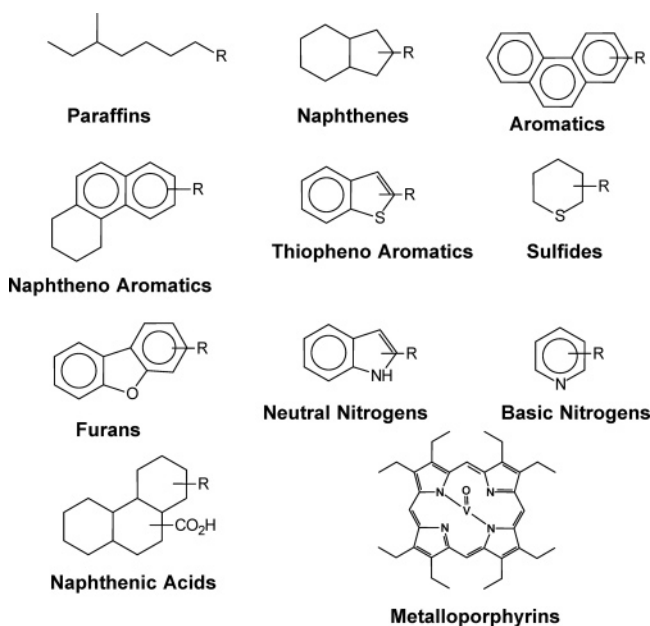

Figure 1. Representative petroleum molecules.

By visual examination, the ESI selectivity shown in Table 1 seems to result from differences in the proton affinities (or gas-phase basicities) of the analyte molecule. Hydrocarbon molecules lack the charge site and have a low probability of forming protonated ions, although aromatic hydrocarbons can interact with some transition-metal ions (soft Lewis acids, such as Ag^+, Pd^{2+}, etc.) to form ion complexes. Acridine has the highest gas-phase basicity, because of the tertiary N atom configuration, and yields the largest ESI response. Note that carbazole and acridine represent two different classes of nitrogen compounds in petroleum; carbazole is normally referenced as a neutral nitrogen species, whereas acridine is referenced as a basic nitrogen species. The results in Table 1 imply that neutral and basic nitrogen molecules may be differentiated by ESI operated under positive- and negative-ion conditions.

A more-detailed investigation indicates that the basicities of the analytes may not be the only factor that affects the ESI responses of the petroleum molecules. Figure 2 shows relative ESI responses of various basic nitrogen model compounds plotted against gas-phase

and liquid-phase basicities of the analytes, respectively. The gas-phase basicities (GBs) were experimental data from the *NIST Chemistry WebBook*,[33] whereas the aqueous basicities (pK_b) were derived from *Lange's Handbook of Chemistry, 14th Edition*.[34] Although the overall trend indicates higher responses for higher basicity molecules, the data are quite scattered and the scatter cannot be rationalized by experimental errors alone. Presently, a widely accepted view is that surface activity has a major role in ESI. High surface activity promotes analyte movement toward the outer layer of the droplet, where it can be preferably evaporated and ionized. The gas-phase reaction may still have an important role in the post-ionization process, where stronger gas-phase bases can extract protons from weak bases and become ionized.

For analytical chemists, it is most important to understand how the ESI process affects the MS response. The extensive works of Kebarle[17] and Enke[26] have shown that a linear dynamic range exists at a concentration of $<10^{-5}$ M. In this region, ESI response is independent of the analyte properties for ionic analytes (preformed ions). The response curves of different analytes merged into a single line. Differences in ionization efficiency become evident only at higher concentrations ($>10^{-5}$ M). This was rationalized by the charge equilibrium model as follows.[26] When the surface concentration of the analytes are much less than that of the electrolytes, the analytes are independently competing with the electrolyte for the surface positions. At higher analyte concentrations, the co-analytes will compete for surface charges. As a result, the analyte with a higher surface activity begins to have a higher surface concentration and ESI response.

The basic compounds in petroleum products are mainly weak bases, such as pyridines, quinolines, and acridines, which behave very differently from the ionic analytes. We have observed a strong influence of matrix conditions (such as pH) and inherent analyte properties (such as surface activity and GBs, etc.) on ESI−MS response. We studied relative ESI response factors for a mixture of seven model compounds over a range of concentrations (Figure 3). The differences in ESI responses are significant but relatively constant for the multiple component mixture at low concentration ($<3 \times 10^{-5}$ M), implying no significant co-analyte interactions in this region. However, the response curves do not merge into a single line as they did in the case of

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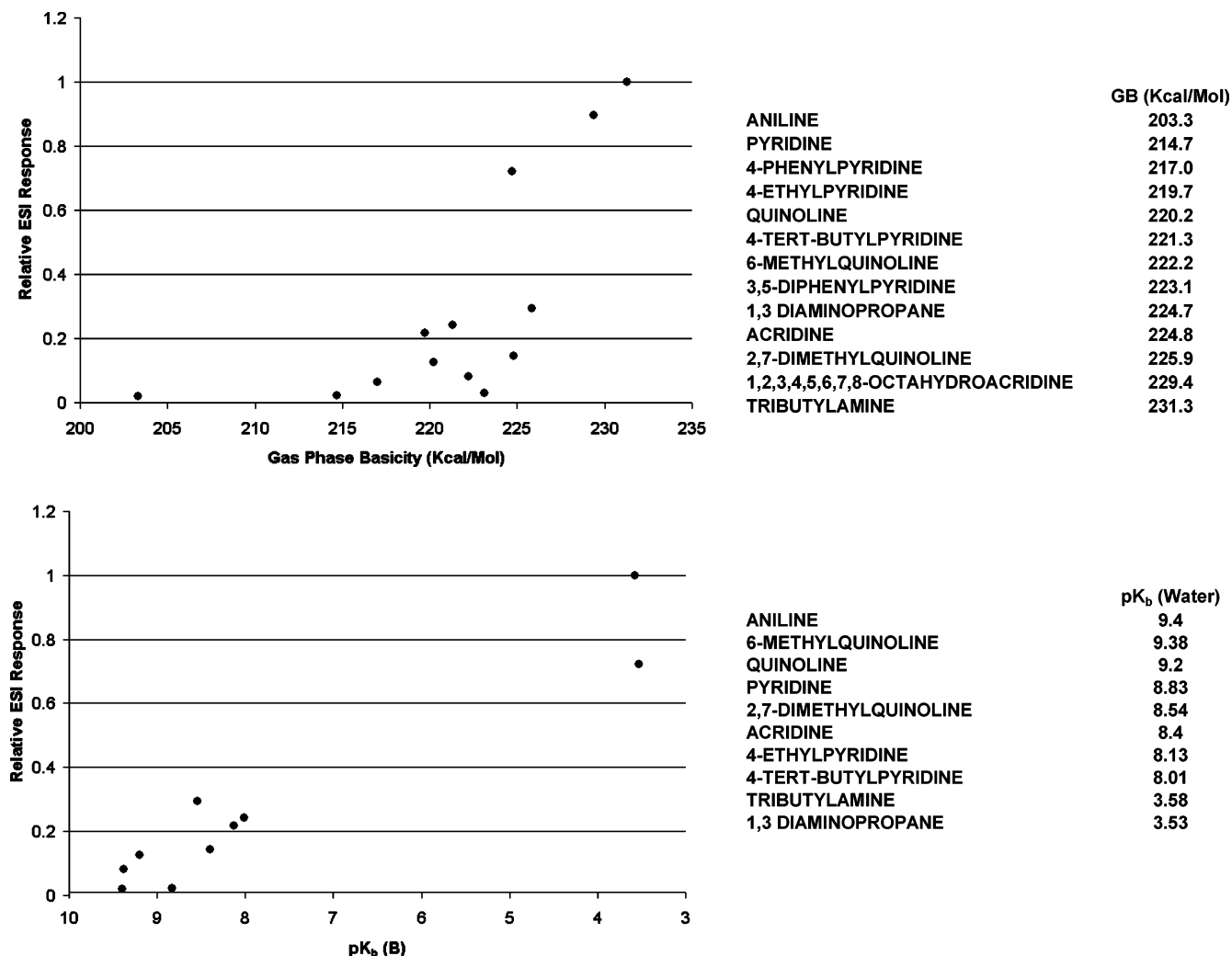(34) Dean, J. A. *Lange's Handbook of Chemistry*, 14th Edition; McGraw-Hill: New York, 1992.

	GB (Kcal/Mol)
ANILINE	203.3
PYRIDINE	214.7
4-PHENYLPYRIDINE	217.0
4-ETHYLPYRIDINE	219.7
QUINOLINE	220.2
4-TERT-BUTYLPYRIDINE	221.3
6-METHYLQUINOLINE	222.2
3,5-DIPHENYLPYRIDINE	223.1
1,3 DIAMINOPROPANE	224.7
ACRIDINE	224.8
2,7-DIMETHYLQUINOLINE	225.9
1,2,3,4,5,6,7,8-OCTAHYDROACRIDINE	229.4
TRIBUTYLAMINE	231.3

	pK_b (Water)
ANILINE	9.4
6-METHYLQUINOLINE	9.38
QUINOLINE	9.2
PYRIDINE	8.83
2,7-DIMETHYLQUINOLINE	8.54
ACRIDINE	8.4
4-ETHYLPYRIDINE	8.13
4-TERT-BUTYLPYRIDINE	8.01
TRIBUTYLAMINE	3.58
1,3 DIAMINOPROPANE	3.53

Figure 2. Electrospray ionization (ESI) responses, as a function of gas-phase basicity (GB) and aqueous basicity (pK_b) (water) of basic nitrogen model compounds; GB values were obtained from the *NIST Chemistry Web Book*[33] and pK_b values were derived from *Lange's Handbook of Chemistry*.[34] Responses are normalized to that of tributylamine. Cone voltage was set 20 V.
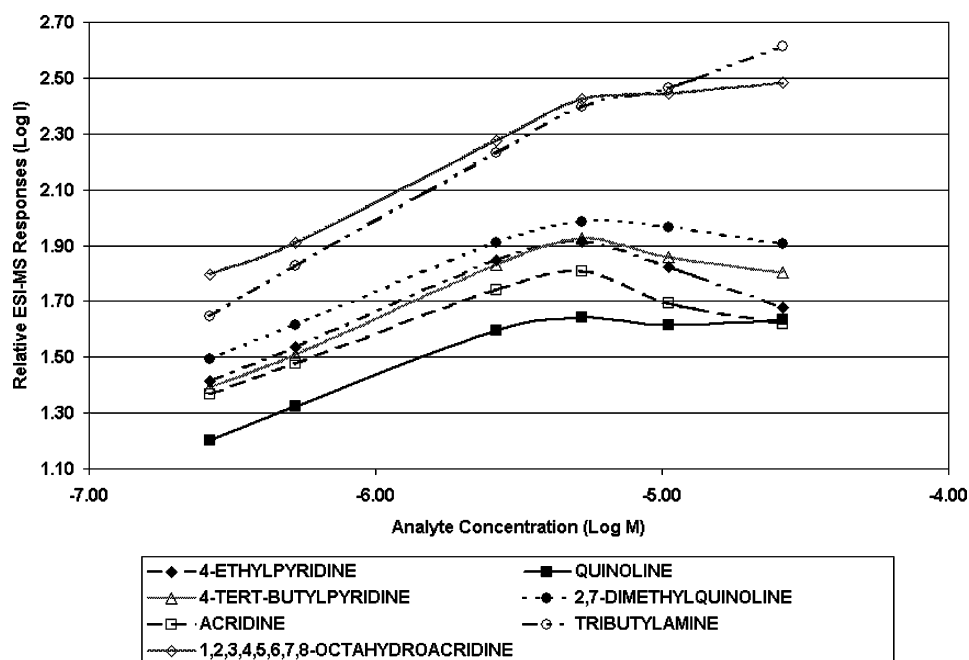
Figure 3. ESI response, as a function of analyte concentration; a linear dynamic range is observed at low analyte concentrations, and analyte interactions are visible at high concentrations. Cone voltage was set at 20 V.
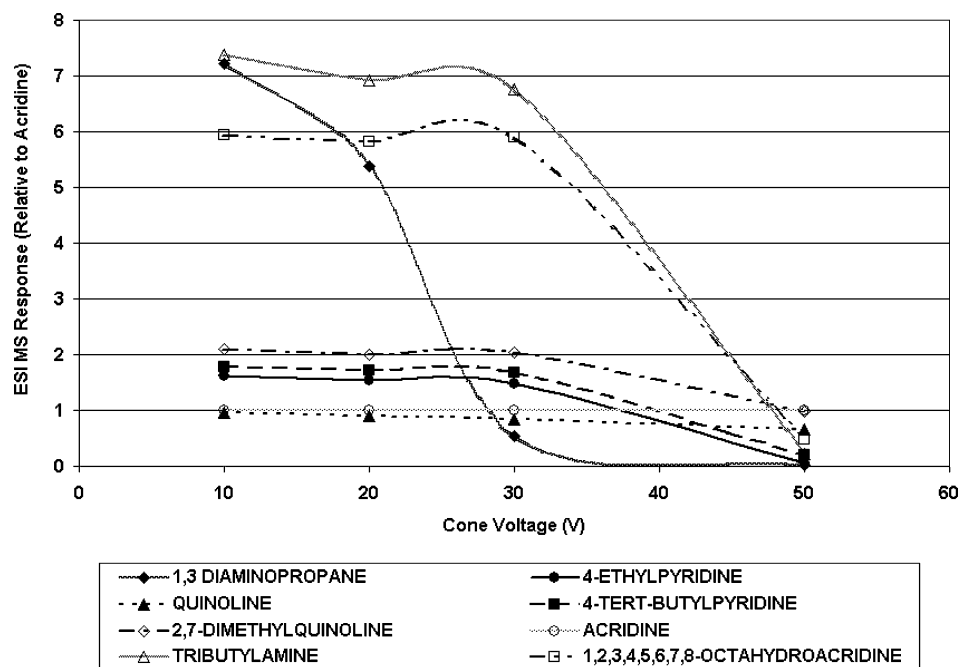
Figure 4. Effect of cone voltages on ESI response. Higher cone voltages induce fragmentations. The effect is particularly significant on aliphatic nitrogen molecules. Responses are normalized to that of acridine.
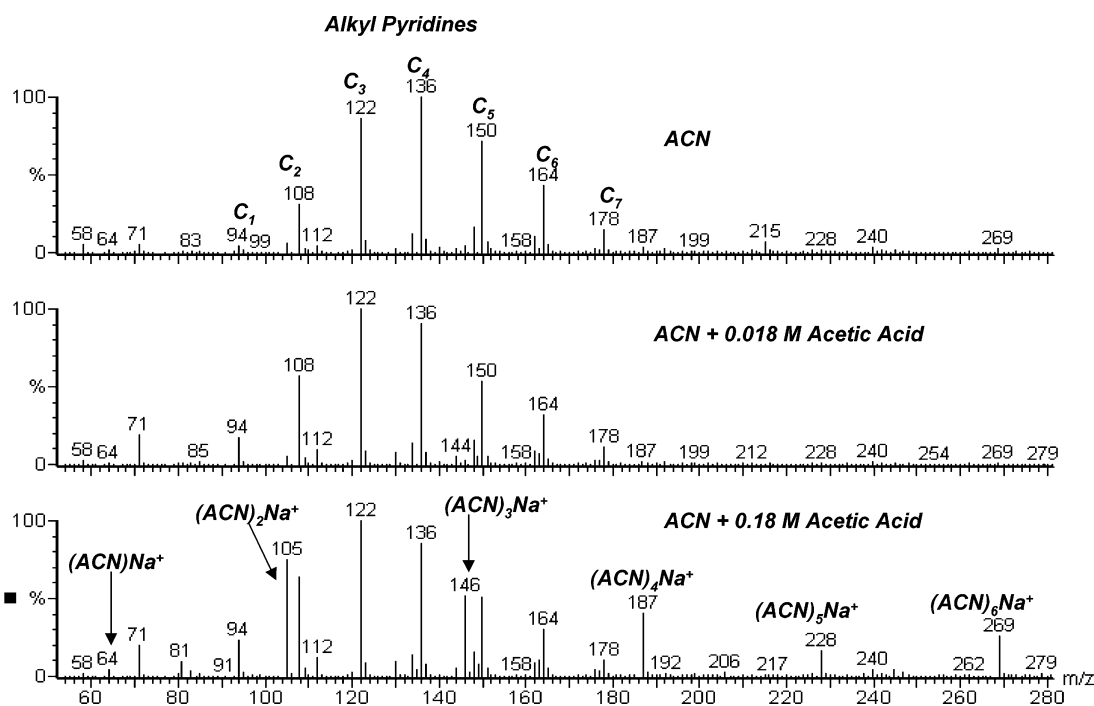

Figure 5. Electrospray ionization mass spectrometry (ESI−MS) spectra of alkyl pyridines in naphtha at three acetic acid levels. The effect of acid level on the ESI−MS spectra is evident. Solvent cluster ions are visible in the 0.18 M acetic acid level.

ionic analytes. The ESI response becomes nonlinear at high analyte concentrations, most likely because of gas-phase ion−molecule reactions. These results suggest that ESI−MS can be used for quantifying mixtures. However, high concentrations (e.g., $>5 \times 10^{-5}$ M) should be avoided.

Collectively, the results in Figures 2 and 3 and the acid effect observed in Figures 5 and 6 (see discussions later in this paper on ESI of petroleum products) suggest that the ESI of petroleum molecules is influenced by variables in both gas-phase (g) and liquid-phase (l)

equilibrium. ESI of petroleum may follow a three-step process as described below:

(1) Protonation in the liquid phase, which is described as

$$B_l + HA_l \rightarrow BH_l^+ + A_l^-$$
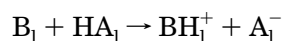
where B is the basic nitrogen compound and HA is an acidic electrolyte (such as acetic acid). The major variables in this step are the pK_b value of the analyte, the pH value of the matrix, and the concentrations of
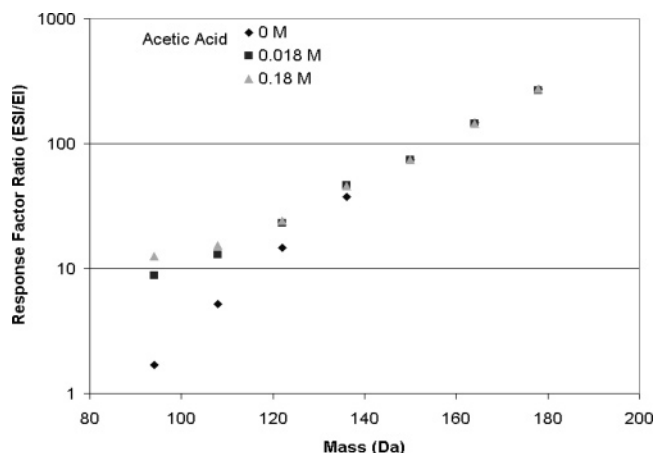
Figure 6. Ratios of ESI $(M + H^+)$/EI (M^+), as a function of molecular weight at three different acid levels; pH has a larger impact on the ESI responses of low-molecular-weight alkyl pyridines.

analytes and electrolyte. The pH effect shown in Figures 5 and 6 suggests that liquid-phase equilibrium had a role in the ESI of nitrogen compounds in petroleum.

(2) Ion evaporation, which is described as

$$BH_l^+ \rightarrow BH_g^+$$
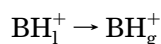
This step is the same as that of the ionic analyte system and has been studied extensively. The major variables in this step are the surface activity and the concentrations of analyte and electrolyte. The step has the most significant impact on the ESI response.

(3) Gas-phase modification, which is described as

$$B_1H_g^+ + B_{2g} \rightarrow B_{1g} + B_2H_g^+$$
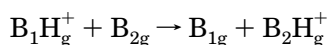
The major variables are the GBs of the solvent and analytes. The effect was observed at high analyte concentrations. One example is the crossover in responses between tributylamine and octahydroacridine, which is shown in Figure 3.

In addition to the inherent molecular properties and matrix conditions described previously, instrumentation configurations and conditions can have significant impact on the ESI responses. The Micromass Quattro-II Z-Spray source requires cone and extraction voltages to guide ions through a Z-path into the quadrupole mass analyzer. It has been known that high cone and extraction voltages can cause collision-induced dissociation of analyte ions prior to their entrance to the mass analyzer. Consequently, they can change the relative responses of analyte ions, because of the collision-induced dissociation (CID) effect and varying stabilities of different analytes. Figure 4 illustrates the impact of cone voltage on the response of various basic nitrogen compounds, relative to acridine. The extraction voltage was set at a constant value of 10 V. Quinoline has a condensed aromatic structure, similar to acridine, and is difficult to fragment. Its ESI response barely changed across a wide cone voltage range (10−50 V). On the other hand, the 1,3-diaminopropane molecular ion is extremely fragile and fragments rapidly under increased cone voltages. The relative responses of most molecules are largely constant, up to 30 V. High cone voltage (50 V) can fragment most molecules and completely change the ESI responses. Extraction voltage has a similar CID effect as the cone voltage. In most of the experiments described in this work, the cone and extraction voltages were set at 30 and 10 V, respectively, to maximize ESI sensitivity and minimize the CID effect. Note that the observations on cone voltage effects were also found on other types of ESI configurations and are not unique to the Quattro Z-Spray source.

Electrospray Ionization of Petroleum Products. Figure 5 shows the ESI−MS spectra of a polar fraction from a naphtha sample obtained at different levels of acetic acid (0 M, 0.018, and 0.18 M). The major mass peak series are consistent with protonated alkyl pyridines. Increasing the acid level altered the alkyl pyridine distributions, particularly on lower-molecular-weight species. It was noted that, at very high acid levels (0.18 M acetic acid), solvent clustering and sodium
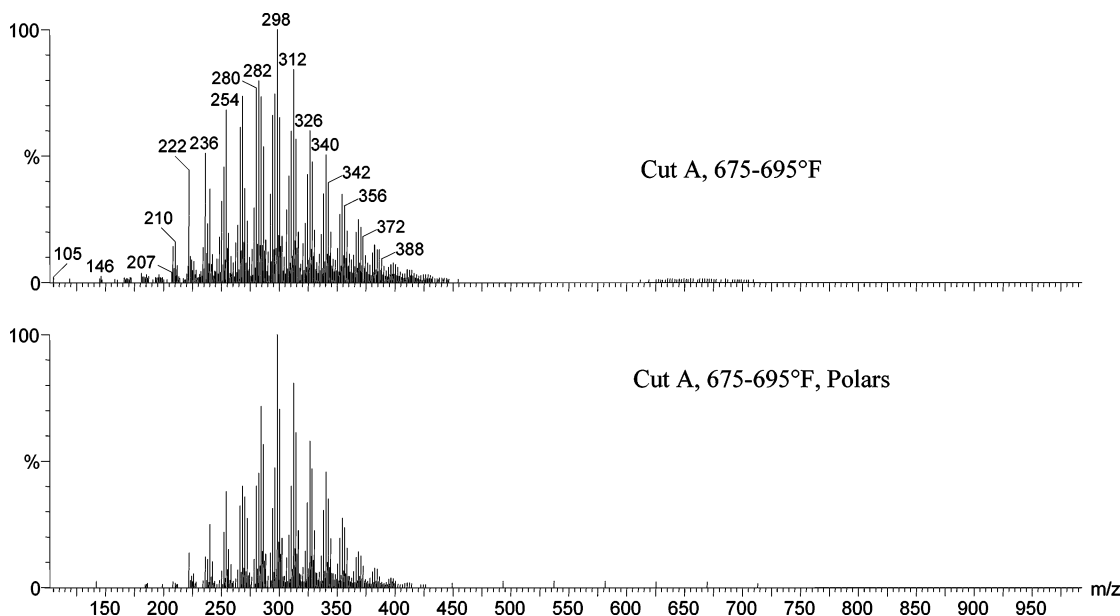

Figure 7. ESI mass profiles of a petroleum distillate (675−695 °F, cut A) and its polar fraction. The mass distributions are very similar, confirming that ESI selectively ionize polars in the hydrocarbon matrix.
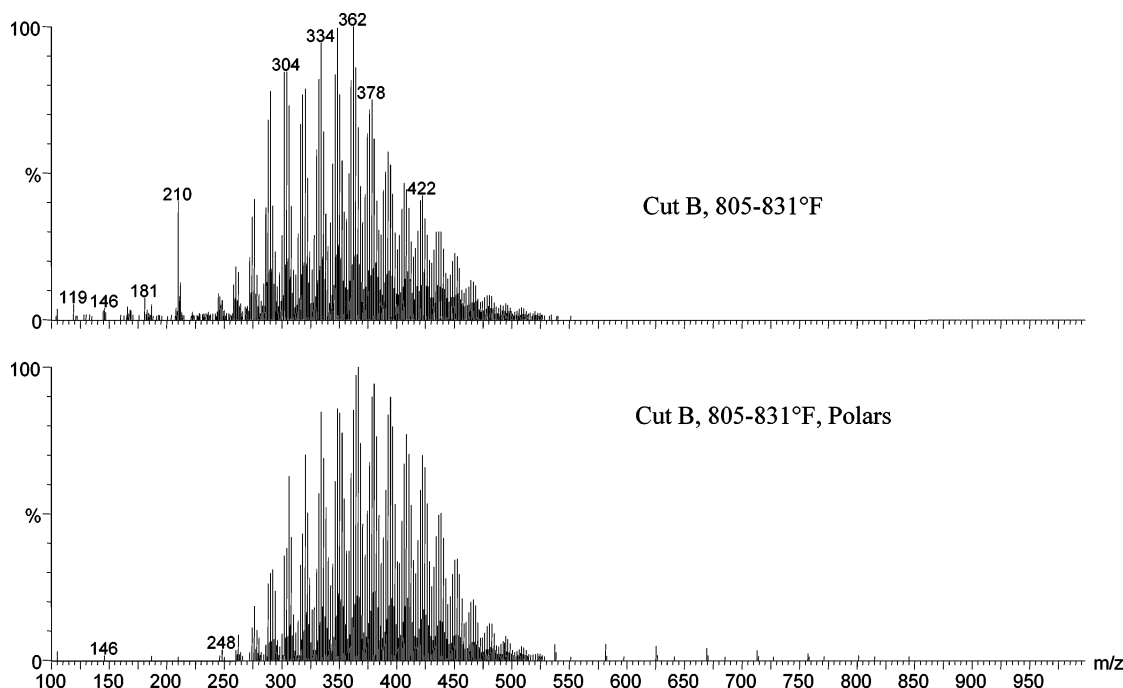
Figure 8. ESI mass profiles of a petroleum distillate (805−831 °F, cut B) and its polar fraction.
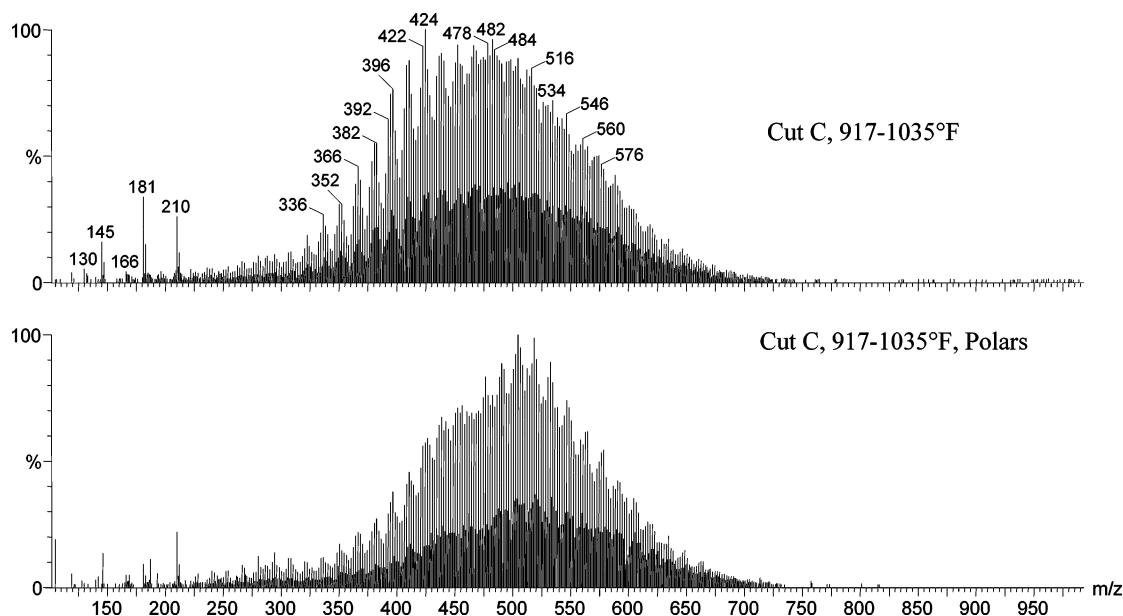

Figure 9. ESI mass profiles of a petroleum distillate (917−1035 °F, cut C) and its polar fraction.

adduction become pronounced and the spectrum becomes more complicated. One plausible explanation is that a high acid level promotes ionization of the solvent molecules by changing the acid−base equilibrium. The data seem to suggest that the sodium adducts of the cluster are more stable than the protonated solvent clusters. The sample was also analyzed via GC−MS under 70 eV EI ionization conditions. EI generates certain $M^{+\bullet}$ ions for C_1-C_7 alkyl pyridines. The impact of acid effect can be better visualized in Figure 6, where the ratios of ESI response $(M + H^+)$ over EI response (M^+) are plotted against the molecular weight of the alkyl pyridines. The acid level significantly affects the ESI responses of lower-molecular-weight species. The effect becomes less apparent as the molecular weight

increases. This observation may be rationalized by the fact that basicities of alkyl pyridines increase as their molecular weights increase. The increase in acid level improved the protonation of low-molecular-weight basic nitrogen compounds. As the degree of alkylation increases, the changes in basicity become small and the pH effect is minimized.

Figures 7−9 illustrate ESI−MS spectra of three petroleum distillates and their polar fractions: 675−695 °F (cut A), 805−831 °F (cut B), and 917−1035 °F (cut C). The molecular-weight profiles of the "as-is" and "polar" fraction are very similar. The average boiling point increases as the average molecular weight of the cuts increases, confirming that ESI−MS can directly provide a molecular-weight distribution of petroleum

Table 2. Mole Fraction of Cut A in Mixtures A−C, Determined by Electrospray Ionization−Mass Spectrometry (ESI−MS)

actual mole fraction of cut A	ESI−MS response of cut A
0.06	0.16
0.21	0.27
0.38	0.43
0.59	0.62
0.79	0.76
0.85	0.82
0.91	0.84

polars. The major mass peaks are even masses, confirming that nitrogen-containing species are predominant.

To evaluate further the impact of molecular weight on ESI response, we mixed the low- and high-boiling gas oil cuts (cuts A and C, shown in Figures 7 and 9) at various concentrations and measured the ESI responses of the series mixtures. Table 2 summarizes the results of ESI molar responses versus the concentrations of the two cuts in the mixture. The ESI responses correlate linearly with the molar concentrations in the range of 0.2−0.8. This observation suggests that ESI does not have severe mass discrimination. This is most likely because petroleum molecules have a tendency to have multiple substitution and long alkylation, which reduces differences in their molecular properties, such as surface activity, gas and liquid-phase basicities, etc.

Conclusions

Basic nitrogen molecules (pyridinic molecules) found in petroleum can be selectively detected using electrospray ionization (ESI). Most other molecular types, such as paraffins, naphthenes, aromatics, and thiophenoaromatics, are largely not ionized via ESI. Metalloporphyrins and neutral nitrogens show little response. The effects of the acid and analyte concentrations, and the instrumental conditions, were evaluated. Increasing the concentration of acid helps the ionization of the low-molecular-weight bases and has minimal impact on higher-molecular-weight species. Analyses of low- and high-molecular-weight petroleum gas oil mixtures showed only limited mass discrimination. Cone and extraction voltages have significant impact on ESI response, particularly on aliphatic amines that can undergo collision-induced dissociation (CID). A linear dynamic range exists at lower analyte concentrations.