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In Situ Raman Spectroscopy of Aza-arenes Adsorbed at the Aqueous/Silica Interface

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Raman spectroscopy is used to study the effect of pH on the solute/sorbent interactions and the chemical nature of the adsorbed species at the aqueous/silica interface for the aza-arenes acridine, quinoline, and pyridine. The neutral aza-arene is hydrogen-bonded to surface sites in aqueous media in which the pH is above the pK_a of the compound. A protonated aza-arene/ClO_4^- ion pair interacts with surface sites in aqueous solutions in which the pH is below the pK_a of the compound. These results may be useful in predicting the fate of these environmentally significant compounds in groundwater.

Index Headings: Raman spectroscopy; Silica adsorption; Aza-arenes.

INTRODUCTION

Pyridine, quinoline, and acridine (Table I) belong to a broader class of compounds called aza-arenes. Aza-arenes are of concern because of their carcinogenic and mutagenic properties.1-10 Aza-arenes are found in tobacco smoke,11,12 automobile exhaust,13 air pollution source effluents,14 shale oil,15 coal tar,16 high-boiling-point petroleum distillates,17 coal liquefaction products,18 recent lake sediments,19 wood preservative wastewater,20 wastewater treatment plant biosludge,21 and contaminated groundwater.22-28

The numerous sources and carcinogenic and mutagenic properties of aza-arenes make the prediction of their transport in groundwater systems a compelling area for research. The ability to predict solute transport in groundwater is critically dependent on understanding interfacial interactions between the solute and the aquifer material (sorbent). The use of Raman spectroscopy is advantageous, because the interfacial region can be explored in situ in aqueous environments similar to those found in natural ground water systems. Data such as the absorbed species stoichiometry, the extent of solute adsorption, and the type of solute/sorbent interactions are needed to predict the fate of contaminants and the most appropriate remediation method.

Previous chromatographic work in these laboratories has established the thermodynamics of the interaction between these aza-arene molecules and silica in solutions of pH above and below the pK_a of these molecules.29,30

The Raman studies reported here are intended to better define the molecular characteristics of the interfaces that are formed at silica in these media.

Previous Raman spectroscopic studies on the effect of pH on solute/sorbent interactions in aqueous environments of pyridine, quinoline, and acridine have been limited to metals as sorbents. Surface-enhanced Raman scattering (SERS) studies of pyridine adsorbed to Ag electrodes31-33 in aqueous alkali halide solutions suggest the presence of two interfacial species. The effect of the aqueous solution pH on the adsorbed species is important only in the presence of Cl^- . A Cl^-/pyridinium ion pair is adsorbed to the Ag through adsorbed Cl^- when both species are present in aqueous solution. The amount of the Cl^-/pyridinium ion pair that is adsorbed decreases as the electrode potential is made more negative due to electrostatic repulsion of the Cl^- . Pyridinium is not an interfacial species when Cl^- is not present, regardless of the aqueous solution pH. The pyridinium releases H^+ upon adsorption, forming neutral pyridine when Cl^- is absent. The neutral pyridine species also adsorbs to the surface in the presence of Cl^- , the Cl^- stabilizing the neutral pyridine species.

SERS investigations of quinoline adsorption on Cu and Ag electrodes in aqueous K_2SO_4 and H_2SO_4 solutions indicate that quinoline also adsorbs as an ion pair through the adsorbed anion when the solution pH is below the pK_a. The adsorption of quinolinium is more prevalent with Cl^- than with SO_4^{2-}.34

The SERS of acridine on Ag colloids35 as a function of bulk aqueous solution pH shows that the neutral species is adsorbed above the pK_a and a Cl^-/acridinium ion pair is adsorbed below the pK_a. The neutral acridine molecule interacts with the Ag surface through the nitrogen lone-pair electrons, and the ion pair adsorbs through adsorbed Cl^- .

More recent studies have reported the Raman spectroscopic behavior of pyridine adsorbed at silica surfaces. In a study by Simpson and Harris, it was found that the interactions between pyridine and silica at the liquid/solid interface are dependent on the amount adsorbed to the surface as determined with the use of Raman spectroscopy.36 Pyridine adsorption to silica from carbon tetrachloride solutions occurs with proton transfer from the
TABLE 1. Selected properties of pyridine, quinoline, and acridine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>Solubility in H₂O (mM)</th>
<th>Kᵢ</th>
<th>pKᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>79.1</td>
<td>-41.6</td>
<td>115.2</td>
<td>Miscible</td>
<td>-5°</td>
<td>5.2°</td>
</tr>
<tr>
<td>Quinoline</td>
<td>129.2</td>
<td>-15</td>
<td>238</td>
<td>49.6°</td>
<td>111°</td>
<td>4.92°</td>
</tr>
<tr>
<td>Acridine</td>
<td>179.2</td>
<td>107-110</td>
<td>346</td>
<td>0.320, 0.214°</td>
<td>2500, 4200°</td>
<td>5.6°</td>
</tr>
</tbody>
</table>

a Reference 1.
b Reference 2.
c Reference 3.
d Reference 4.
e Reference 5.

surface, the degree of proton transfer decreasing as surface coverage increases.

The deposition of pyridine from the vapor phase onto silica has also been studied extensively by Raman spectroscopy. The region of the pyridine spectrum that has been most studied is that containing the pyridine ring-breathing vibrational modes. These vibrational modes are sensitive to the strength of the interaction of the lone-pair electrons of the pyridine nitrogen with the surface. The stronger the interaction, the larger the positive shift in the totally symmetric ring-breathing mode frequency. Physisorbed pyridine, hydrogen-bonded pyridine, and Bronsted acid interactions have all been identified through their discrete positions of this vibrational band.

More generally, previous surface Raman spectroscopic studies on aza-arenes indicate that more than one species can be adsorbed to the surface. Interfacial species observed include the neutral species, a Cl⁻/protonated aza-arene cation pair, and the protonated aza-arene cation. The particular interfacial species existing in a given system depends on the presence of electrolytes, the aqueous solution pH, the extent of surface coverage, and the chemical composition of the surface. Work to date has not dealt with the adsorption of aza-arenes at silica surfaces from aqueous environments or the effect of electrolytes on these adsorption processes. The necessity of studying aza-arene adsorption at silica from aqueous environments, as opposed to adsorption at metal electrodes or gas-phase adsorption, is due to the fact that the former most closely approximates the conditions in a saturated groundwater system. Thus, the objectives of this research are to identify the interfacial species in these aza-arene systems and to characterize their solute/sorbent interactions as a function of pH in solutions containing electrolytes commonly found in groundwater systems. Porous silica is used as a model aquifer material (sorbent), because it is well characterized chemically and physically and because it is a major constituent of aquifer materials.

EXPERIMENTAL

Sample Preparation. Batch experiments were used to adsorb the aza-arenes to the sorbent. The aza-arene concentrations used were 1.00 M for pyridine (pH 6.7, 3.6), 0.0392 and 0.0765 M for quinoline (pH 7.1, 4.0), and 0.279 and 2.98 mM for acridine (pH 7.0, 4.0). The buffer and electrolyte concentrations were 0.01 M Na₂HPO₄ and 0.02 M NaClO₄, respectively. The pH of the solutions was adjusted with HClO₄ or NaOH. The solutions were added to 5-mL glass vials with Teflon®-lined caps to which the sorbent was then added. The solid-to-solution (v:v) ratio was ~1:13. The vials were equilibrated for 24 h by agitation on a rotating rack. The bulk solution was removed from the sorbent by vacuum filtration for ~5 min through a 0.45-μm filter. The sorbent was then packed into glass capillary tubes (1.5-mm o.d.), and the ends sealed by heating with a flame.

Raman Spectroscopy. The spectrum of each sample was taken in seven regions that were ~350 cm⁻¹ wide (300-650, 610-960, 820-1170, 950-1300, 1230-1580, 1430-1780, and 2875-3225 cm⁻¹). Peak frequencies were accurately determined by calibration of the spectrometer with standards (indene, toluene, or imidazole) immediately prior to acquisition of the sample spectrum. Multiple experiments on these standards and on pyridine showed that the precision in frequency determination is ±2 cm⁻¹.

A sloping background was observed in many of the raw spectra due to the response characteristics of the detector. This background was removed with the use of an automatic baseline-correction program provided as part of the SpectraCalc spectral data processing software.

The spectra were obtained with laser excitation at 600 nm provided by Ar⁺-laser (Coherent Radiation Innova 90-5) pumping of a dye laser (Coherent CR-599) containing a Rhodamine 6G/ethylene glycol solution. Plasma and fluorescent lines of the laser beam were removed with a bandpass filter (Pomfret Research Optics, Inc.) with a 3-nm bandpass. A Spex 1877 Triplet telescope spectrograph with gratings in the filter stage of 600 grooves mm⁻¹ and that in the spectrographic stage of 1200 grooves mm⁻¹ was used. A Nikon f/1.4 camera lens (50-mm size) was used to collect the scattered radiation at 90° to the sample, which was then focused onto the entrance slit of the Triplet. The light incident on the sample was perpendicularly polarized and at 90° to the camera lens. The positioning of the sample was accomplished by an x-y-z translation stage with micrometer adjustments. A Photometrics, Ltd. PM512 charge-coupled device (CCD) consisting of 512 columns by 512 rows of pixels, each 20 μm on a side, was used for detection. The CCD was housed in a Model CH210 camera head from Photometrics, Ltd., which allows operation at -110°C. The CCD images were processed with a Photometrics RDS200 system equipped with a custom version of SpectraCalc.

Sorbent. The sorbent was porous silica (PQ XG-20, PQ Corp.) with an average particle diameter of 125 μm, an average pore diameter of 20 nm, and a specific surface area of 230 m² g⁻¹ (N₂ BET as reported by the manufacturer). The silica was washed successively with methanol, pentane, methanol, 1.0 M HCl, and distilled, deionized water, and dried at 105°C.

Reagents. Acridine (Kodak reagent grade), quinoline (Kodak reagent grade), pyridine (Aldrich HPLC grade).
and pentane (Fisher HPLC grade) were used as received. Methanol (EM Science GR grade) was distilled before use. Water used in all experiments was deionized and distilled over potassium permanganate and vacuum filtered through a 0.45-μm membrane filter (Millipore Corp.). NaOH (J. T. Baker analyzed reagent) and HClO₄ (Fisher certified ACS) were used to control the pH. NaH₂PO₄ (EM Science GR grade) was used as a buffer, and anhydrous NaClO₄ (Aldrich) was used as an electrolyte.

**RESULTS**

Interactions between the aza-arene solutes and the silica adsorbent are determined by comparing the spectrum of the adsorbed species to the spectrum from an appropriate model environment of the aza-arene. Several models of the aza-arenes were chosen, depending on the interfacial environment that was being modeled. The model environments used here for physisorption of the aza-arenes at silica surfaces are the neat liquid (pyridine and quinoline) and solid (acridine). Physisorption interactions are expected to be very weak, resulting in essentially no perturbation of the aza-arene vibrational response observed for the pure compounds.

The model environment chosen for hydrogen bonding of the aza-arenes with silica surfaces is aqueous solutions of the aza-arene with a pH above the pKₐ of the compound. Under these solution conditions, the nitrogen atom of the aza-arene remains unprotonated and is available for hydrogen bonding with water or hydroxyl ions. Such interactions result in minor spectral changes in the vibrational spectrum of these molecules. This environment for the aza-arene is expected to accurately model the interactions of unprotonated aza-arenes with surface-bound water or surface silanols at silica surfaces.

The model environment used here for protonated aza-arene (a Bronsted acid) adsorption at silica through an ion pair interaction is an aqueous electrolyte solution of the protonated aza-arene cation at a pH below the pKₐ of the compound. Protonation of these aza-arenes confers significant changes on the vibrational spectrum of the molecule that are signatory for the protonated form. The protonated aza-arene can be involved in ion pair formation with anions held at the silica surface by strong hydrogen-bond formation.

The vibrational frequencies of the aza-arene in the different model environments and in the adsorbed state are compared; if similar, the interactions in the two systems are assumed to be alike.

**Pyridine.** Previous Raman spectroscopy studies on pyridine have demonstrated that the vibrational response of this molecule is very sensitive to its chemical environment. Significant changes in the Raman spectral response are observed for pyridine in solutions of different pH and ionic content relative to the behavior observed for neat pyridine. The Raman bands observed for the model environments studied here and the silica interfacial species are listed and assigned in Table II. Representative spectra for interfacial pyridine species at pH values above and below the pKₐ are shown in Figs. 1 and 2 for the regions 820–1170 cm⁻¹ and 1430–1780 cm⁻¹, respectively. The frequencies for the pyridine spectra (Table II) suggest a different interaction between the pyridine and the silica when the solution pH is above the pKₐ compared to when it is below the pKₐ for all seven spectral regions probed.

Comparison of the spectra from the 820–1170 cm⁻¹ region (Fig. 1) is particularly useful, since the ring-breathing modes at 991 and 1030 cm⁻¹ in neat pyridine have been shown to be extremely sensitive to chemical environment. In general, the totally symmetric ring-breathing mode at 991 cm⁻¹ increases in frequency as the strength of interaction of the ring nitrogen atom lone-pair electrons with other species (e.g., hydrogen-bond donors, Lewis acid sites) increases. In the spectra for the hydrogen-bonding model environment (pH above the pKₐ), the ring-breathing modes shift to 1002 and 1033 cm⁻¹, respectively, and the intensity in energy presumably being due to the formation of the hydrogen bond with the nitrogen atom making the ring-breathing modes slightly more difficult. For the Bronsted acid/ion pair model environment (pH below the pKₐ), these modes are observed at 1009 and 1023 cm⁻¹. Thus, significant spectral shifts relative to neat pyridine are observed for solution pyridine upon simple hydrogen bonding of the molecule with water; even larger spectral changes are noted relative to hydrogen-bonded pyridine upon protonation. The changes noted here are consistent with those previously reported in the literature.

In the spectra of interfacial pyridine, when the aqueous solution pH is below (top spectrum in Fig. 1) and above (bottom spectrum in Fig. 1) the pKₐ, the totally symmetric mode is observed at 1009 cm⁻¹ at a pH of 3.6 and at 1003 cm⁻¹ (with a noticeable shoulder at 1011 cm⁻¹) at pH 6.7. The relatively low frequency of the band at 1003 cm⁻¹ indicates a much weaker interaction between the pyridine and the silica at pH 6.7 than at pH 3.6. On the other hand, the shoulder at 1011 cm⁻¹ is indicative of a more strongly interactive pyridine species, but the lower relative intensity suggests one that is not as prevalent as the more weakly bound species. A band at 934 cm⁻¹ is observed at pH 3.6 due to the presence of ClO₄⁻ in the

| TABLE II. Raman spectral data (frequencies in cm⁻¹) for pyridine. |
|-----------------|-----------------|-----------------|
|                 | pH = 6.7        | pH = 3.6        |
|                 | W/o sorbent     | With sorbent    | W/o sorbent     | With sorbent    | Assignment      |
| 603             | 618             | 619             | 613             | 611             | IP ring def²    |
| 650             | 649             | 650             | 636             | 629             | IP ring def     |
| 991             | 1002            | 1003,1011 (sh)  | 1009            | 1009            | Totally symmetric ring breathing |
| 1030            | 1033            | 1033            | 1023            | 1026            | Trigonal symmetry ring breathing |
| 1066            | 1064            | 1063            | 1058            | 1054            | IP C-H bend     |
| 1219            | 1217            | 1216            | 1205            | 1201            | IP C-H bend     |
| 1482            | 1487            | 1488            | 1494            | 1494            | r(C-O)             |
| 1578            | 1576            | 1577            | 1620            | 1618            | r(C-O)             |
| 1597            | NO              | 1595            | NO              | 1647            | Overtone         |
| 3059            | 3074            | 3080            | 3118            | 3116            | r(C-H)            |

² Solutions contained 1.0 M pyridine, 0.01 M NaH₂PO₄, and 0.02 M NaClO₄.  
³ From Refs. 41 and 42.  
⁴ IP = in-plane mode.  
⁵ def = deformation.  
⁶ r = stretch.  
⁷ Not observed.
interface. No band due to $\text{ClO}_4^-$ is observed at pH 6.7, even though $\text{ClO}_4$ is in the pH 6.7 solution from which the pyridine adsors. The trigonal-symmetry ring-breathing mode is observed at 1023 cm$^{-1}$ at pH 3.6, but at 1033 cm$^{-1}$ at pH 6.7.

A similar comparison in the 1430–1780 cm$^{-1}$ region shows that differences exist between the model environment spectra when the aqueous solution pH is below and above the $pK_a$ of pyridine. The bands of interest in this region are the $\nu$(C–C) at 1482 and 1578 cm$^{-1}$ and an overtone mode at 1597 cm$^{-1}$. The data for the model environments in Table II and the spectra from the silica surfaces in Fig. 2 demonstrate similar changes in these bands as the pH is changed. In both the model solution and silica surface spectra, these bands shift to higher frequencies by ~7, 44, and 52 cm$^{-1}$, respectively, as the solution pH is lowered from 6.7 to 3.6.

The single band observed in the $\nu$(C–H) region at 3059 cm$^{-1}$ is also sensitive to solution pH, increasing in frequency as the strength of interaction of the nitrogen atom lone-pair electrons increases. A similar trend is observed in both the model solution environment and the silica surface spectra obtained here. This band is shifted to higher frequencies by ~40 cm$^{-1}$ as the solution pH is lowered.

Finally, the in-plane (IP) ring-deformation modes at 603 and 650 cm$^{-1}$ and the IP C–H bend at 1219 cm$^{-1}$ are shifted to lower frequencies as the pH is decreased. This behavior is in contrast to all the ring C–C modes (except for the trigonal-symmetry ring-breathing mode at 1030 cm$^{-1}$), which are shifted to higher frequencies. In total, the frequency shifts suggest that the interaction of pyridine with silica at a solution pH below the $pK_a$ is similar to the interaction represented by the Bronsted acid/ion pair model environment, and the interaction of pyridine with silica at a solution pH above the $pK_a$ is similar to the model environment for hydrogen bonding.

There are differences between the model environment
TABLE III. Raman spectral data (frequencies in cm\(^{-1}\)) for quinoline.

| Neat quinoline | pH = 7.1 W/o sorbent | With sorbent | pH = 4.0 W/o sorbent | With sorbent | Assignment
|---------------|----------------------|--------------|----------------------|--------------|------------------|
| 520           | 521                  | 522          | 519                  | 519          | IP ring def \(^a\)
| 757           | 762                  | 764          | 767                  | 768          | IP ring def \(^a\)
| 1009          | 1010                 | 1010         | 1010                 | 1012         | IP C-H bend
| 1029          | 1036                 | 1035         | 1050                 | 1051         | Ring breathing \(^a\)
| 1371          | 1375                 | 1373         | 1384                 | 1383         | \(\nu(C-O)_{aq}\) \(^b\)
| 1393          | 1398                 | 1394         | 1395                 | 1396         | \(\nu(C-O)_{aq}\) \(^b\)
| 1432          | 1437                 | 1436         | 1438                 | 1438         | IP C-H bend \(^a\)
| 1501          | 1508                 | NO\(^b\)     | 1496                 | 1494         | \(\nu(C-O)_{aq}\) \(^b\)
| 1570          | 1579                 | 1582         | 1605                 | 1604         | Central \(\nu(C-C)\) \(^b\)

\(^{a}\) Solutions at pH 7.1 and 4.0 contained 0.0392 M and 0.0765 M quinoline, respectively; all solutions contained 0.01 M Na\(_2\)HPO\(_4\) and 0.02 M NaClO\(_4\).

\(^{b}\) From Ref. 43

\(^{c}\) IP = in-plane mode.

\(^{d}\) def = deformation.

\(^{e}\) v = stretch.

\(^{f}\) Not observed.

spectra and the adsorbed species spectra at both pH values, however. At pH 6.7, the \(\nu(C-H)\) is observed at 3074 cm\(^{-1}\) in the model environment, but at 3080 cm\(^{-1}\) for adsorbed pyridine. At pH 3.6, differences between the model environment and the adsorbed pyridine are observed in the IP ring-deformation mode at 650 cm\(^{-1}\), the trigonal-symmetry ring-breathing mode at 1030 cm\(^{-1}\), the IP C-H bending mode at 1219 cm\(^{-1}\), and the IP C-H bending mode at 1066 cm\(^{-1}\). All these modes in the silica surface spectra are shifted to lower frequencies at pH 3.6 relative to the model spectra, except the trigonal-symmetry ring-breathing mode.

**Quinoline.** The Raman bands observed for the model environments and the silica interfacial species are listed and assigned\(^b\) in Table III. Changes in the Raman spectral response are observed for neutral quinoline in aqueous solution (pH above the pH\(_K_a\)) relative to neat quinoline. In addition, changes in the Raman spectral response are observed upon quinoline protonation that are similar to those observed for pyridine. Representative Raman spectra for quinoline model environments and silica interfacial species are shown in Figs. 3 and 4. The spectra in Fig. 3 are in the 820–1170 cm\(^{-1}\) region for quinoline at the silica interface at pH 7.1 (top), the pH 7.1 aqueous model environment (middle), and neat quinoline (bottom). Figure 4 shows Raman spectra in the 1230–1580 cm\(^{-1}\) region for the interfacial quinoline species in solutions of pH below (top spectrum) and above (bottom spectrum) the pH\(_K_a\).

Significant differences between the spectra for the neat quinoline and the pH 7.1 and 4.0 model environments are observed for the IP ring-deformation mode (757 cm\(^{-1}\)), the ring-breathing mode (1029 cm\(^{-1}\)), \(\nu(C-C)\) modes (1371 and 1501 cm\(^{-1}\)), the IP C-H bending mode (1432 cm\(^{-1}\)), and the central \(\nu(C-C)\) mode (1570 cm\(^{-1}\)). In the solution spectra, the vibrational bands at 757, 1029, 1371, 1432, and 1570 cm\(^{-1}\) are shifted to higher frequencies as the pH is decreased. The remainder of the bands are shifted to lower frequencies, except for the 1009-cm\(^{-1}\) band, which is not shifted.

Differences between the spectra of the interfacial species at pH values above and below the pH\(_K_a\) are observed for the IP ring-deformation mode (757 cm\(^{-1}\)), the ring-breathing mode (1029 cm\(^{-1}\)), the \(\nu(C-C)\) mode (1371 cm\(^{-1}\)), and the central \(\nu(C-C)\) mode (1570 cm\(^{-1}\)). The \(\nu(C-C)\) vibration observed at 1494 cm\(^{-1}\) at pH 4.0 for interfacial quinoline is not observed at pH 7.1. The spectrum of the interfacial quinoline species at pH 7.1 is similar to the hydrogen-bonding model environment. Interestingly, ClO\(_4^-\) is observed in the interface at these pH values, as evidenced by the band at 938 cm\(^{-1}\). This frequency is shifted to higher values by 4 cm\(^{-1}\) in the interfacial spectrum relative to its solution value. For pH 4.0, the interfacial quinoline environment appears similar to that of the Bronsted acid/ion pair model environment.

**Acridine.** The results for acridine are somewhat more limited, because acridine is a weaker Raman scatterer than pyridine or quinoline. Moreover, the low solubility of acridine (~1 mM) limited the quality of data that could be obtained.
The Raman bands observed for the model environments and the interfacial species are listed and assigned in Table IV. Figure 5 shows representative Raman spectra in the 1230–1580 cm⁻¹ region for interfacial acridine species for solution pH values below (top spectrum) and above (bottom spectrum) the pKₐ. Figure 6 shows representative Raman spectra in the 1430–1780 cm⁻¹ region for the interfacial species at pH 4.0 (top spectrum), the model environment at pH 4.0 (middle spectrum), and solid acridine (bottom spectrum). The spectral data suggest that the aza-arene solute/silica sorbent interactions are slightly different when the aqueous solution pH is above and below the pKₐ. Small differences between the ν(C–C) modes (1400 and 1476 cm⁻¹) at the two pH values are noteworthy. The spectra of the model acridine environments for hydrogen bonding (pH 7.0) and Brønsted acid/ion pair interaction (pH 4.0) are similar to those of the interfacial species when the solution pH is above and below the pKₐ, respectively.

Fig. 4. Raman spectra of adsorbed quinoline species in the region 1230 to 1580 cm⁻¹ with 260-mW laser power and 360-s integration time: (a) pH 4.0; (b) pH 7.1.

Fig. 5. Raman spectra of adsorbed acridine species in the region 1230 to 1580 cm⁻¹ with 225-mW laser power and 400-s integration time: (a) pH 4.0; (b) pH 7.0.

TABLE IV. Raman spectral data (frequencies in cm⁻¹) for acridine.  

<table>
<thead>
<tr>
<th>Solid acridine</th>
<th>W/o sorbent</th>
<th>With sorbent</th>
<th>W/o sorbent</th>
<th>With sorbent</th>
<th>Assignment¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>NO</td>
<td>NO</td>
<td>401</td>
<td>399</td>
<td>IP² ring def¹</td>
</tr>
<tr>
<td>1400</td>
<td>1405</td>
<td>1406</td>
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<td>1409</td>
<td>ν(C–C)₁₆₂</td>
</tr>
<tr>
<td>1476</td>
<td>1500</td>
<td>1497</td>
<td>1496</td>
<td>1492</td>
<td>ν(C–C)₁₄₆</td>
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<tr>
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<td>NO</td>
<td>1593</td>
<td>1592</td>
<td>ν(C–C)₁₄₅</td>
</tr>
<tr>
<td>pH = 4.0</td>
<td></td>
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<tr>
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<td>NO</td>
<td>NO</td>
<td>742</td>
<td>755</td>
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<td>1400</td>
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<td>1409</td>
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<td>1592</td>
<td>ν(C–C)₁₄₅</td>
</tr>
</tbody>
</table>

¹ Solutions at pH 7.0 and pH 4.0 contained 0.279 mM and 2.98 mM acridine, respectively; all solutions contained 0.01 M Na₂HPO₄ and 0.02 M NaClO₃.
² From Ref. 44.
³ Not observed.
⁴ IP = in-plane mode.
⁵ def = deformation.
⁶ ν = stretch.
**DISCUSSION**

The Raman spectral results generally support the contention that these aza-arenes interact with the silica surfaces in a manner dictated by the protonation state of the aza-arene. These results are best discussed in the context of independent measures of interaction of these solutes with the silica surfaces based on previous chromatographic studies in these laboratories.

**Adsorption Thermodynamics.** Previous results from liquid chromatography experiments, shown in Table V, suggest that the adsorption of pyridine, quinoline, and acridine to porous silica similar to that used in these experiments is greater when the solution pH is below the pK_a than above. This effect is indicated by a more negative free energy of adsorption at pH values less than the pK_a. Furthermore, the enthalpy of the adsorption reaction is more exothermic when the solution pH is above the pK_a than below, and the entropy is larger when the solution pH is below the pK_a than above. The enthalpy of adsorption becomes less exothermic and the entropy of adsorption decreases in the order acridine > quinoline > pyridine.

The extent of adsorption follows the order acridine > quinoline > pyridine when the solution pH is below the pK_a. However, when the solution pH is above the pK_a, the adsorption of pyridine is slightly greater than that of quinoline. The change in the aqueous solubility of the aza-arenes as a function of ring number does not account for the trend in the extent of adsorption, because the van't Hoff plots for the aza-arenes do not overlap when the extent of adsorption is normalized for solubility differences, as shown in Fig. 7. Thus, the increase in the extent of adsorption with ring number appears to be due to the increased overlap of the molecule with potential adsorption sites.

Similar trends for these molecules are observed for adsorption to Cu and Ni electrodes and to montmorillonite and smectite clays. Furthermore, the strong adsorption of aza-arenes at alumina surfaces has been similarly related to the free energy of adsorption at these surfaces. Aza-arenes can interact with these surfaces at several types of sites, leading to an increased adsorption of these molecules.

**Sampling the Interfacial Region.** In attempt to define the interfacial region, the surface speciation of silica as a
The function of pH can be estimated with the use of SURFEQL\textsuperscript{52} from the following equilibria:\textsuperscript{53,54}

\[
\square > \text{SiOH} = \square > \text{SiO}^- + \text{H}^+ \\
pK_a = 6.8
\]

(1)

\[
\text{Na}^+ + \square > \text{SiOH} = \square > \text{SiO}^- \text{Na}^+ + \text{H}^+ \\
pK_a = 7.0
\]

(2)

with the use of a constant-capacitance model (capacitance
\[= 1.25 \text{ F m}^{-2}\]) of the electric double layer (Fig. 8). In
these equations, \[\square > \text{SiOH}\] represents the hydroxylated
silica surface. The first reaction describes the Brønsted
acid behavior of surface silanol groups. The second rea-
action describes the exchange of \[\text{Na}^+\] for \[\text{H}^+\]. This latter
reaction has been observed to be important in adsorption
thermodynamics in past column chromatography experi-
ments.\textsuperscript{39,40} The fraction of total surface silanols that
are protonated varies from 85% at pH 7 to 99.9% at pH 4.
The fraction of deprotonated silanol sites reaches a max-
imum of 10% at pH 8; those deprotonated silanols asso-
ciated with a \[\text{Na}^+\] maximize at 5%.

Silica surfaces that are fully hydroxylated and im-
mersed in water are purely hydrophilic and exhibit no
hydrophobic characteristics.\textsuperscript{55} Hydrophilic silica sur-
faces are defined to be those that bind water molecules with
an energy greater than the heat of liquefaction, 10.5 kcal mol\textsuperscript{-1}.\textsuperscript{56} The energy of a single hydrogen bond between
a silanol group and a water molecule is only slightly larger
than that of a single hydrogen bond in water, ~6.0 kcal
mol\textsuperscript{-1}. However, the potential for multiple hydrogen
bond formation exists, which results in complete coverage
of surface silanols by water. Moreover, the water mole-
cules adsorbed on this first layer of water molecules are ad-
sorbed even more strongly as a result of multiple hydro-
gen bonding. The adsorption of an aza-arene molecule
directly to surface silanol groups in aqueous systems would
necessitate the desorption of all \[\text{H}_2\text{O}\] molecules interac-
ting with the surface. Although this behavior intuitively
seems unlikely, the question of direct adsorption of aza-
arenes to surface silanol sites cannot be resolved with the
available data. Therefore, both surface-adsorbed water
and silanol groups will be considered as potential ad-
sorption sites for aza-arenes in this study.

Several aspects of the experimental Raman data sup-
port the contention that the interfacial response is being
probed here. The Raman bands associated with silica that
are observed in these studies at 800 and 980 cm\textsuperscript{-1} are
direct evidence that the spectroscopy samples the inter-
facial region between the bulk liquid and the silica surface.
The 980-cm\textsuperscript{-1} band is assigned to the \[\nu(\text{Si-OH})\] vibra-
tion.\textsuperscript{57} The 800-cm\textsuperscript{-1} band is assigned to the \[\nu(\text{Si-O-Si})\]
mode for bulk silica.\textsuperscript{58,59} Furthermore, the frequency shifts
in some of the spectral bands of the adsorbed species
relative to those of the model environments also suggest
that the interfacial region is being sampled. Such shifts
would not be expected if the bulk solution is responsible
for the Raman spectral response.

**Solute/Sorbent Interactions.** Differences between the
Raman spectra of the aza-arene in the model environment
and the interface are interpreted to be indicative of dif-
fferences in chemical environment. By analogy, similari-
ties between the spectra of the model environment and
the interface are interpreted in terms of similarities be-
tween the environments. The spectra presented above
are discussed in this light.

**Pyridine.** At pH 6.7, the only vibrational band for in-
terfacial pyridine that differs significantly from the hy-
drogen-bonding model environment is the \[\nu(\text{C-H})\] at 3059
cm\textsuperscript{-1}. This band is shifted to higher frequencies by ~6
\text{ cm}^{-1} in going from the model environment to the inter-
face. The enthalpy of adsorption for pyridine is ~5.21 ±
0.02 kcal mol\textsuperscript{-1}. This value is probably not sufficient
to displace interfacial water molecules to allow the pyridine
to adsorb directly to a surface silanol group. Hence, the
interfacial pyridine most likely interacts with surface-ad-
sorbed water, forming hydrogen bonds through the ni-
trogen lone-pair electrons. In this picture, the environ-
ment after adsorption is expected to be similar to that in
the model environment. The increase in frequency of the
\[\nu(\text{C-H})\] suggests a slight increase in the interaction energy
of the nitrogen lone-pair electrons for the interfacial pyr-
idine relative to the model environment. Similar conclu-
sions have been drawn for N-methyl derivatives of pi-
peridine, pyridine, and morpholine adsorbed to silica.\textsuperscript{60}

In pyridine solutions at pH 3.6, small shifts in peak
position are observed for certain bands in going from the
model spectrum to that of the interface. Small shifts in
frequency to lower values of 7, 4, and 4 \text{ cm}^{-1} are noted for
the IP ring-deformation mode at 650 \text{ cm}^{-1} and the IP C-H
bending modes at 1066 and 1219 \text{ cm}^{-1}, respectively,
although a shift to higher frequency of 3 \text{ cm}^{-1} is
observed for the trigonal-symmetry ring-breathing mode.
The shifts to lower frequency suggest some loss of double-
bond character in the ring and/or a much more restricted
environment. Previous studies have shown that the ad-
sorption of benzene to Au surfaces results in large (20–
30 \text{ cm}^{-1}) shifts to lower frequency of the totally sym-
metric and other ring-breathing modes, indicating strong
\[\pi\] adsorbate/surface interactions.\textsuperscript{61} The much smaller shifts
observed here for pyridine imply a much weaker inter-
action between the pyridine \[\pi\] electrons and the surface.
One possible picture of the adsorbed state consistent with
weaker \[\pi\]-electron interaction is interaction of these elec-

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trons through dipole–dipole forces with the hydrogen atoms of adsorbed water, thereby reducing the electron density of the ring and the bond strength. Similar interactions with water have been suggested previously for the aromatic compounds benzene and thiophene. Hydrogen bonding of benzene to water has also been suggested, in which the electrons of the benzene ring act as a hydrogen-bond acceptor and the hydrogen atoms of water act as hydrogen-bond donors. The binding energy for this interaction was estimated to be 1.78 kcal mol⁻¹.

The shifts to lower frequency observed in the spectra of the interfacial pyridine relative to the model at pH 3.6 may also indicate that pyridinium adsorbs as an ion pair with ClO₄⁻. The ClO₄⁻ may interact with interfacial water molecules and the pyridinium with the ClO₄⁻ through dipole–dipole and electrostatic forces. The small enthalpy of adsorption (−3.82 ± 0.01 kcal mol⁻¹) suggests that interaction of pyridine or pyridinium directly with surface silanol groups is unlikely. In addition, no change in the spectral behavior of the interfacial ClO₄⁻ relative to the model environment is observed, suggesting that ClO₄⁻ is in a similar environment in the interface and in the bulk solution. The adsorption of a pyridinium/ClO₄⁻ ion pair is consistent with previous SERS investigations of pyridine adsorption to Ag electrodes as a function of the aqueous solution pH.31–33

Quinoline. At pH 7.1, shifts are observed in the spectra for the 1393-cm⁻¹ ν(C–C) and the 1570-cm⁻¹ central ν(C–C) in going from the model to the interfacial environment for quinoline. A change in the frequency of the ClO₄⁻ band for the interfacial species relative to the model environment species is also observed at both pH values. The small changes in peak positions for quinoline at pH 7.1 and the lack of changes at pH 4.0 indicate that both the model and interfacial environments are similar at both pH values.

The enthalpies of adsorption (Table V) for quinoline at pH 7.1 and 4.0 are −5.41 ± 0.01 kcal mol⁻¹ and −5.81 ± 0.01 kcal mol⁻¹, respectively. These values are not sufficiently exothermic to suggest the direct adsorption of quinoline to surface silanol groups. Thus, the interaction of quinoline with surface-adsorbed water is expected, thereby causing only a slight perturbation of the environment of quinoline.

The ClO₄⁻ band is shifted to higher frequencies at both solution pH values by 4 cm⁻¹, suggesting a small change in its environment, possibly its involvement in ion pair formation. The interfacial environment would be different from the model environment if ClO₄⁻ interacted with surface-adsorbed water and formed ion pairs with quinolinium at pH 4.0. Quinolinium/Cl⁻ ion pairs have been previously proposed to absorb to Ag and Cu electrodes at solution pH values below the pK₆ of quinoline.34 Our experimental results further indicate that ClO₄⁻ is in the interfacial region even when the aza-arene is not in solution. Therefore, ClO₄⁻ may also help to stabilize neutral quinoline in the interface when the solution pH is greater than the pK₆.

Acridine. Several changes are observed in the spectra for acridine. The 1476-cm⁻¹ ν(C–C) from the interfacial species is shifted to lower frequencies by several cm⁻¹ in comparison to the model environments at pH 4.0 and 7.0. In addition, the ν(C–C) at 1556 cm⁻¹ exhibits a small shift to lower frequencies at pH 4.0. These small shifts are similar to the shifts observed for pyridine and quinoline. The adsorption enthalpy for acridine is weakly exothermic (Table V) at both pH 7.0 (−8.05 ± 0.01 kcal mol⁻¹) and pH 4.0 (−6.95 ± 0.01), similar to pyridine and quinoline; therefore, the direct interaction of acridine with surface silanol groups is unlikely. Collectively, these results suggest that the interfacial and bulk environments are similar, consistent with the small frequency shifts observed for acridine in the two environments. The picture of the interface that emerges from these data is that neutral acridine hydrogen bonds with the interfacial water at pH values above the pK₆ similar to pyridine and quinoline. Previous work has demonstrated that neutral acridine adsorsb to Ag sols through the nitrogen lone-pair electrons.33 Such an interaction is not possible between the acridine and silica surface silanol groups due to the weakly exothermic nature of the adsorption.

The similarity between the acridine spectra of the model environment and adsorbed species at pH 4.0 suggests that the interfacial species is an acridinium/ClO₄⁻ ion pair. A similar acridinium/Cl⁻ ion pair has been observed to be adsorbed at Ag surfaces from solutions of comparable pH.35 Presumably, this ion pair involves the Cl⁻ directly bonded to the Ag surface with weak interactions between the aromatic π electrons and the surface.35 The small shift of the acridine ring modes observed here suggests similar weak interactions for this system.

Species in the Interfacial Region. The results of these Raman spectroscopy studies suggest that the neutral forms of the aza-arene molecules are adsorbed when the solution pH is above the pK₆ of the compound. Adsorption of the neutral molecule is expected at these pH values, since it is the dominant species present in solution (pyridine, pH 6.7, 96.8%; quinoline, pH 7.1, 99.3%; acridine, pH 7.0, 96.2%). ClO₄⁻ is observed in the interfacial spectra of the neutral molecules and also when the aza-arenes are not present. Vibrational bands from phosphate are observed in the spectra without the sorbent, but not in the spectra with the sorbent. This observation may indicate that phosphate is not adsorbed and/or that the phosphate bands are too weak to be observed.

The protonated aza-arene cations and ClO₄⁻ are proposed as the major interfacial constituents for solutions below the pK₆ of the compounds on the basis of thermodynamic data from liquid chromatography experiments and the Raman spectroscopic data. The enthalpies of adsorption for acridine and pyridine are more exothermic when the solution pH is above the pK₆ than below, suggesting that hydrogen bonding of the neutral molecule with adsorption sites is stronger than the interaction energy of the ion pair. Two adsorption geometries for the ion pair can be envisioned. The ion pair may adsorb with the cation between the ClO₄⁻ and the surface and/or with the ClO₄⁻ interacting directly with interfacial water between the cation and the surface. The former adsorption geometry would rely on weak dipole–dipole interactions between the π electrons of the aromatic rings and the hydrogen atoms of interfacial water molecules to hold the ion pair at the surface. The latter orientation would be based on hydrogen-bonding interactions between surface-adsorbed water and the ClO₄⁻. This arrangement would place the aza-arene cation further from the surface, there-
by diminishing the strength of aza-arene π-electron/interfacial water interaction. Although an exact determination of orientation is not possible on the basis of these experimental data, the fact that the $\text{ClO}_4^-$ is observed in the interfacial spectra even in the absence of aza-arenes is a strong argument in favor of the latter adsorption geometry. In any case, on the basis of the adsorption enthalpies, both orientations are predicted to result in interactions between the protonated aza-arenes and the surface that are weaker than those associated with the hydrogen-bonded neutral molecule.

The free energies for adsorption are greater for solution pH values below the $pK_a$ of the compounds than above. In light of the enthalpies of adsorption discussed above, these results suggest that a smaller loss of entropy is incurred for adsorption of the protonated forms of the aza-arenes than for adsorption of the neutral aza-arenes. This postulate is consistent with the entropy data in Table V. These observations might be rationalized as follows: The localized nature of the hydrogen-bonding interaction between the nitrogen lone-pair electrons of the aza-arenes and interfacial water at pH values above the $pK_a$ results in a more structured interface in which rotational orientation of the adsorbed aza-arene is restricted. The interactions of the cation/$\text{ClO}_4^-$ ion pairs with the surface below the $pK_a$, although weaker, result in a much less structured interface. The slightly greater free energies of adsorption for the protonated aza-arene cations suggest that more cations are adsorbed than neutrals, possibly due to the strong hydrogen-bonding tendencies of $\text{ClO}_4^-$.

The Raman spectroscopic results are also consistent with the adsorption of cation/$\text{ClO}_4^-$ ion pairs at pH values below the $pK_a$. The spectra of all aza-arenes show small but significant shifts to lower frequencies of certain ring vibrations at these pH values. Fewer bands exhibit such shifts for pH values above the $pK_a$. Collectively, these observations suggest that the interaction of the aza-arenes with the surface is through the cation ring π electrons (dipole-dipole) below the $pK_a$ and mainly through the nitrogen lone-pair electrons above the $pK_a$. The fact that the spectra from the interfacial and model environments are similar suggests that the aza-arene species in the two environments are similar. The picture described is consistent with this similarity in each pH region.

In total, the adsorption of aza-arenes at silica surfaces is characterized by the following reaction for the neutral molecules (M):

$$\text{M} - \text{H}_2\text{O} + \text{SiOH-H}_2\text{O} = \text{SiOH-H}_2\text{O-M} + \text{H}_2\text{O} \quad (3)$$

and for the cation $(\text{MH}^+)/(\text{ClO}_4^-)$ ion pair:

$$\text{MH}^+\text{ClO}_4^- - \text{H}_2\text{O} + \text{SiOH-H}_2\text{O} = \text{SiOH-H}_2\text{O-ClO}_4^-\text{MH}^+ + \text{H}_2\text{O}. \quad (4)$$

The first reaction is hydrogen bonding of the neutral species to adsorbed $\text{H}_2\text{O}$ on the surface through the nitrogen lone-pair electrons. This reaction is shown schematically for acridine in Fig. 9. The second reaction represents adsorption of the hydrated cation/$\text{ClO}_4^-$ ion pair, shown schematically for acridine in Fig. 10. The stoichiometry of the ion pair is assumed to be 1:1 on the basis of electroneutrality considerations.

Despite the level of molecular detail of these pictures, several aspects of the interfacial chemistry in these systems are not known on the basis of the data in hand. The number of water molecules solvating the aza-arenes (ion pair and neutral species) in solution and at the surface, the number of water molecules displaced from the surface due to solute adsorption, and the number of solute molecules at each adsorption site are all unknown at this time. Thus, although the Raman spectroscopy has been useful in helping to elucidate the molecular characteristics of these interfaces, more work is needed before a complete picture can be developed.
30. R. A. Matzner and R. C. Bales, Chemosphere, in press.