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Determination of the Ion-Pair Constant between Chloride Ion and Cationic-Coated, Silver SERS Substrates Using Competitive Complexation

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The interaction of chloride ion with cationic-coated silver surface-enhanced Raman scattering (SERS) substrates was monitored using a competitive complexation technique. In this approach, the nitrate concentration is kept constant and the chloride ion concentration is varied. The change in the nitrate peak area, ΔA_{NO_3} , is measured as a function of chloride ion concentration, C_{Cl} . The measured response is described by the following relationship: $\Delta A_{\text{NO}_3} = VC_{\text{Cl}}/(K + C_{\text{Cl}})$. Using the value of K and the value of the ion-pair constant between the cationic coatings and nitrate ion, it is possible to extract the value of the ion-pair constant for chloride ion. The selectivities of the cationic coatings for nitrate, sulfate, and chloride ions are discussed.

1. Introduction

Thiols react on silver and gold surfaces to form self-assembled monolayers (SAMs).^{1–3} Formation of SAMs has been used to chemically modify electrodes⁴ and surface acoustic wave (SAW) devices⁵ so that they will respond to a particular compound or class of compounds. On roughened silver and gold substrates, surface-enhanced Raman scattering (SERS) spectra can be obtained for these SAMs.^{3,6–7} Carron and Hurley³ demonstrated that SERS spectra can be used to measure the axial and azimuthal angles of phenylthiolates adsorbed on noble-metal surfaces. From such measurements, the orientation of the molecule on the surface can be deduced. Using SERS, Carron et al. were able to monitor the complexation of Pb^{2+} , Cd^{2+} , and Cu^{2+} with a 4-(2-pyridylazo)resorcinol disulfide derivative⁶ and the interaction of alkali metal ions with a thiol-derivatized dibenzo-18-crown-6.⁷ The alkali metals, Pb^{2+} , Cd^{2+} , and Cu^{2+} do not exhibit Raman active bands. However, complexation of these ions with the thiol coatings resulted in changes in the spectra of the coating. By monitoring these changes in the spectral features as a function of metal ion concentration, the formation constant of complexation could be determined.

Recently, Mosier-Boss and Lieberman⁹ demonstrated that the interaction between nitrate and sulfate with cationic thiols could be monitored by SERS. Both nitrate and sulfate exhibit a Raman active band. These anions do not adsorb directly onto the bare metal due to the presence of the cationic SAM. However, enhancement in the Raman

signals of nitrate and sulfate is observed as these anions interact with the cationic coatings on the SERS substrate. It is not clear whether the increase in the signal intensity of the anion peaks is due to concentration of the analyte at the interface, or to SERS, or to both. This ambiguity exists because the SERS phenomenon persists beyond the first layer of adsorbed molecules¹⁰ and does not require physical contact between the adsorbate molecule and the metal surface. By directly monitoring the magnitude of the Raman signal due to nitrate and sulfate as a function of anion concentration, Mosier-Boss and Lieberman⁹ measured the ion-pair constants between these anions and the cationic thiols under investigation.

Not all analytes exhibit Raman active modes. This was the case for the metal ions investigated by Carron et al.^{6,7} Nor does interaction between the analyte and coating guarantee that there will be significant measurable changes in the spectral features of the coating. For example, the interaction between the anions and the cationic thiols is electrostatic in origin and did not result in any new features appearing in the SERS spectra of the coatings.⁹ In instances where the analyte does not exhibit a Raman signal and the spectrum of the coating changes minimally upon complexation, it may be possible to obtain the formation constant between the analyte and coating using a competitive approach. Competitive complexation has been used routinely to evaluate the complexation constants of macrocyclic ligands with heterocyclic cations,¹² alkylammonium ions,^{12,13} and metal ions that do not have useful NMR nuclei.¹⁴ Recently, equilibrium constants for the complexation between nitrate and lanthanide cations were determined using a competitive technique involving xylitol, which forms 1:1 complexes with lanthanide cations.¹⁵ Boss and Popov¹⁶ showed that

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formation constants larger than 10^4 and 10^5 M^{-1} could be measured by NMR through the technique of competitive complexation.

We are currently developing sensor technology to monitor anion concentrations in aqueous environments. There is considerable interest in the detection of nitrate, sulfate, and phosphate ions due to their implication in eutrophication of ponds and lakes¹⁷ and increased incidences of red tide.¹⁸ The sensor technology under development involves SERS of cationic-coated substrates.⁹ It was, therefore, of interest to us to determine the strength of interaction between chloride ion and the cationic-coated SERS substrates. Chloride ion does not exhibit a Raman active vibrational mode. Nor did we observe significant changes in the spectral features of the cationic coating upon complexation with either nitrate or sulfate ion.⁹ In this communication, we demonstrate that competitive complexation can be used to obtain the ion-pair constant between chloride ion and cationic-coated SERS substrates.

2. Experimental Section

2.1. Reagents. Sodium nitrate (Johnson Matthey), sodium chloride (Aldrich), and sodium sulfate (Aldrich) were used as received. Aqueous solutions were prepared using deionized water. In these experiments, the nitrate concentration was kept constant at 1000 ppm and the chloride ion concentration was varied between 0 and 10^5 ppm. The pH of the anion solutions is 5.0. The thiols, (dimethylamino)ethanethiol hydrochloride (Aldrich), 2-mercapto-4-methylpyrimidine hydrochloride (Avocado Research Chemicals), cysteamine hydrochloride (Fluka), (diethylamino)ethanethiol hydrochloride (Fluka), and L-cysteine ethyl ester hydrochloride (Fluka), were used as received.

2.2. Preparation of SERS Substrates. An insulated copper wire was soldered to a 1 cm length of 2 mm diameter silver wire (99.9%, Aldrich). The 2 mm diameter silver wire was potted inside a 5 mm diameter glass tube with a chemically resistant epoxy (Epoxy Patch 1C, Hysol).

Prior to use the Ag disk of the electrode was electrochemically roughened in the manner described by Weaver et al.¹⁹ Using a PAR 173 potentiostat under computer control, the silver electrode was roughened in a 0.1 M KCl solution by applying 25 successive oxidation–reduction cycles (ORC)¹⁹ from -300 to $+1200$ mV vs the Ag/AgCl reference electrode at a sweep rate of 500 mV s^{-1} . For each scan, the potential was held for 1.3 s at the positive limit and 30 s at the negative limit. After electrochemical roughening, the electrode was rinsed with water (HPLC grade, Aldrich) and then ethanol (HPLC grade, Aldrich). The electrode was immersed in a dilute thiol solution in ethanol and allowed to react for approximately 24 h to form a self-assembled monolayer. Before use the substrates were thoroughly rinsed with ethanol and stored in water between uses.

2.3. Evaluation of Cationic-Coated SERS Substrates. Figure 1 shows a schematic of the flow-through cell used to evaluate the concentration response of cationic-coated, SERS substrates to nitrate, sulfate, and chloride. The body of the flow-through cell is constructed of Teflon. A 25 mm diameter, 2 mm thick sapphire disk was used as the optically transparent window. A Kel-F window retainer holds the window in place. An O-ring provides a leak-tight seal between the window and the cell body. While a Teflon bushing holds the SERS substrate in place, another O-ring provides a leak-tight seal around the glass tube of the electrode. The inlet and outlet consist of 20 gauge stainless steel tubing that has been epoxied in place using a chemically resistant epoxy (Epoxy Patch 1C, Hysol). Besides being constructed of chemically resistant materials, the cell has a low volume (~ 0.5 mL).

Raman measurements were made using the Raman Solution 852 system (Detection Limit). The Raman Solution 852 is comprised of a 100 mW DBR, frequency-stabilized, diode laser

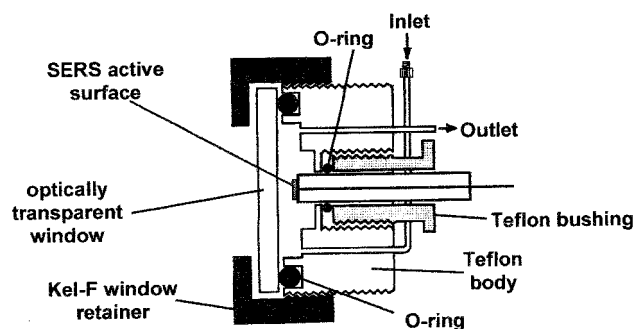


Figure 1. Schematic of the flow-through cell used to evaluate the concentration response of cationic-coated, silver SERS substrates to nitrate, sulfate, and chloride.

operating at 852 nm and a fiber-optic miniature Raman probe. The spectral resolution is on the order of $7\text{--}8 \text{ cm}^{-1}$. The laser, spectrograph, and CCD are integrated in a 13 in. \times 7 in. \times 9 in. enclosure having a volume less than 0.5 ft^3 . The miniature probe houses the appropriate filters to remove the interferences due to Raman emissions in the optical fibers. The excitation and collection fibers are $50 \mu\text{m}$ in diameter. The spectrograph has an f number of 2, 1200 grooves/mm grating, and a TE cooled Kodak 0400 CCD. Data collection and operation are controlled by a 133 MHz Pentium-based lap-top computer. The flow-through cell is held rigidly in place with the "Opti-Claw" optical mount (New Focus, P/N 9832). The Opti-Claw is mounted on an x,y -translation stage. The fiber-optic probe of the Raman system is mounted on a laboratory jack (Newport, P/N 270) which is used to adjust the z -axis. Experimental conditions are noted in the figure captions.

2.4. Computer Modeling of Thiol-Coated Silver Substrates. Molecular modeling of the thiol-coated silver substrates was done using Alchemy III, a molecular modeling software package from IBM. Within Alchemy, a graphical form of Dreiding model construction allows accurate and flexible manipulations of structure. Once a molecule is built, the Alchemy minimizer performs a conjugate gradient minimization on a force field equation which is dependent on the positions of the atoms of a selected molecule. The potential energy of the molecule is the sum of the following terms

$$E = E_{\text{str}} + E_{\text{ang}} + E_{\text{tor}} + E_{\text{vdw}} + E_{\text{oop}} + E_{\text{ele}} \quad (1)$$

where all E 's represent the energy values corresponding to the given types of interactions. The subscripts denote bond stretching (str), angle bending (ang), torsion deformation (tor), van der Waals interaction (vdw), out of plane bending (oop), and electrostatic interactions (ele). Within the minimizer, the molecular coordinates are modified to obtain reasonable, low-energy, molecular geometries. Once minimized, the molecule can be depicted as a space-filling model in which each atom is represented by a sphere of radius equal to its van der Waals radius. All computations were carried out on a Pentium computer operating at a 166 MHz clock speed.

3. Results and Discussion

3.1. Normal Raman and SERS Spectra of Cysteamine Hydrochloride. Previously, Bryant and Pemberton^{20,21} had obtained normal Raman spectra of solid and liquid 1-alkanethiols as well as SERS spectra of self-assembled monolayers formed from 1-alkanethiols on silver and gold surfaces. They observed that the $\nu(\text{C-S})$ region between 600 and 750 cm^{-1} provides conformational information about the C–C bonds adjacent to the C–S bond in the alkanethiol. For example, two peaks are observed in the C–S stretching region in the Raman

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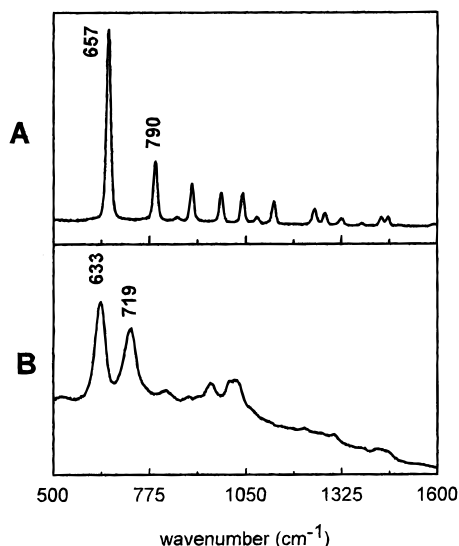


Figure 2. Comparison of the (A) normal Raman and (B) SERS spectra of cysteamine hydrochloride (CY). Both spectra were obtained using 852 nm excitation (laser power is 50 mW at the sample). The normal Raman spectrum is obtained for the solid thiol using a 20 s acquisition time. The SERS spectrum is obtained on a silver substrate using a 6 s acquisition time.

spectrum obtained for solid 1-butanethiol.²¹ The peak at 652 cm⁻¹ is assigned to the gauche (G) conformer while the peak at 729 cm⁻¹ is assigned to the trans (T) conformer. Upon adsorption onto a silver or gold substrate, the frequencies for both $\nu(\text{C-S})$ bands decrease considerably— $\nu(\text{C-S})_{\text{G}} = 632 \text{ cm}^{-1}$ and $\nu(\text{C-S})_{\text{T}} = 706 \text{ cm}^{-1}$ on gold²¹ and $\nu(\text{C-S})_{\text{G}} = 630 \text{ cm}^{-1}$ and $\nu(\text{C-S})_{\text{T}} = 699 \text{ cm}^{-1}$ on silver.²⁰ For 1-butanethiol, adsorption onto gold and silver occurs through the thiol group.

Figure 2 shows normal Raman and SERS spectra obtained for cysteamine hydrochloride (CY). The normal Raman spectrum of CY in the solid state exhibits only one peak in the C-S stretching region at 657 cm⁻¹. Using the assignments of Bryant and Pemberton, this band is attributed to the gauche conformer. No peaks are observed near 730 cm⁻¹, which is where the peak due to the trans conformer should occur. The peak at 790 cm⁻¹ is assigned to a CH₂ rocking mode.²⁰ The absence of a trans conformer was surprising since, for steric reasons, the trans conformation, in which the amine and thiol groups are as far apart as they can be, is usually more stable. However, other factors, such as dipole-dipole interactions and hydrogen bonding, can affect the relative stability of conformations. The stability of the gauche conformer over the trans is, therefore, attributed to intramolecular hydrogen bonding between the thiol and amine groups of CY.

In contrast to the normal Raman spectrum, the SERS spectrum of CY on silver exhibits two peaks in the C-S stretching region. The peak at 633 cm⁻¹ is assigned to the gauche conformer while the peak at 719 cm⁻¹ is attributed to the trans conformer. Since the $\nu(\text{C-S})_{\text{G}}$ is shifted to lower frequency compared to $\nu(\text{C-S})_{\text{G}}$ in the solid state, as was observed for 1-butanethiol,^{20,21} we can conclude that CY binds to silver through the thiol group. It is unlikely that the NH₃⁺ group of CY interacts with the metal surface. If the NH₃⁺ group did interact with the metal surface, we would have expected to see additional peaks in the C-S stretching region at higher frequencies than those peaks shown in Figure 2b. Furthermore, although it has been demonstrated that amine and cyanide

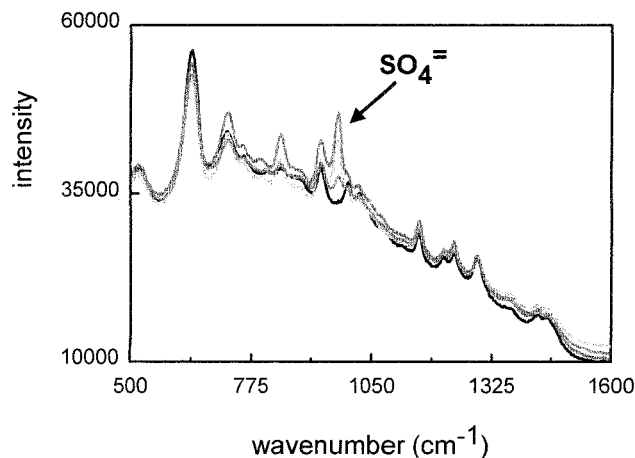


Figure 3. SERS spectra of Ag/DMA obtained using 852 nm excitation (power at the sample is 50 mW) and 15 s acquisition times. Sulfate ion concentrations are 0, 25, 500, and 2500 ppm.

functional groups bind to gold and silver particles,²² it has also been shown that adsorption of HS-(CH₂)₁₀CH₂-X (where X = CN, COOH, OH) onto gold is preferentially through the thiol group.²³

3.2. Interaction of Cationic-Coated Silver SERS Substrates with Nitrate and Sulfate. In this investigation, the cationic thiols used are cysteamine hydrochloride (CY), (dimethylamino)ethanethiol hydrochloride (DMA), 2-mercapto-4-methylpyrimidine hydrochloride (MMP), (diethylamino)ethanethiol hydrochloride (DEA), and L-cysteine ethyl ester hydrochloride (CYE). The adsorption of nitrate and sulfate on silver SERS substrates chemically modified by these cationic thiols was examined.⁹ Figure 3 shows SERS spectra obtained for Ag/DMA in the presence of sulfate ion. We can clearly see the evolution of the sulfate peak at 982 cm⁻¹ as the anion interacts with the coating. It is known that anions that adsorb strongly to surfaces can enhance SERS spectra.^{24,25} The enhancement arises from the static electric field dependence of the polarizability. The absence of changes in the spectrum of the cationic coating in the presence of nitrate and sulfate anions rules out an anion effect. Similar conclusions were reached by Heynes et al.⁷ in their SERS study of the interaction of alkali metals with a thiol-derivatized dibenzo-18-crown-6. For Ag/DMA, the $\nu(\text{C-S})_{\text{G}}$ occurs at 640 cm⁻¹ and $\nu(\text{C-S})_{\text{T}}$ at 723 cm⁻¹ (Figure 3). No change in the ratio of the intensities of the peaks due to the C-S stretching modes of the gauche and trans conformers is observed in the presence of increasing sulfate ion concentration. This indicates that the coating does not undergo conformational changes in the presence of sulfate ion. Since no new peaks occur in the spectrum of the coating in the presence of sulfate ion, we can conclude that any changes in the structure of the coating upon the addition of sulfate ion are minor.

The concentration response between sulfate and the Ag/DMA substrate is shown in Figure 4. At low sulfate concentration, the peak area increases linearly with concentration. At higher solution concentrations of anion,

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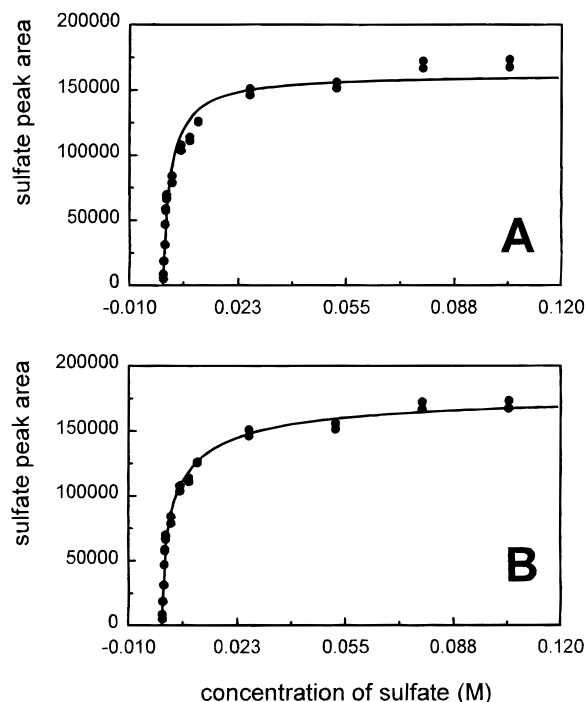
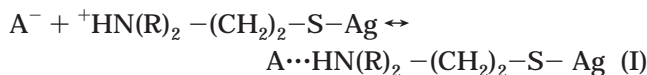


Figure 4. Sulfate peak area plotted as a function of sulfate ion concentration for the Ag/DMA system. The concentration response has been modeled using a Langmuir isotherm (A) and a Frumkin isotherm (B).

the response levels off as the adsorption sites on the substrate become fully occupied. The concentration profile shown in Figure 4 is typical for the interaction between the cationic thiols and either nitrate or sulfate ion. The reaction between the anion (A^-) and cationic-coated SERS substrate ($^+HN(R)_2-(CH_2)_2-S-Ag$) is given by



We used both a Langmuir isotherm, Figure 4A, and a Frumkin, Figure 4B, to model the concentration response between Ag/DMA and sulfate. The Langmuir isotherm is given by

$$\theta = \frac{CK}{1 + KC} \quad (2)$$

and the Frumkin isotherm is

$$\theta = \frac{CKe^{2g\theta}}{1 + Ke^{2g\theta}} \quad (3)$$

where θ is the fractional coverage of sulfate on the coated substrate, K is the ion-pair constant between nitrate and the coating, C is the solution concentration of sulfate, and g is the Frumkin parameter. The Frumkin parameter takes into account interactions between the adsorbed species. For both the Langmuir and Frumkin isotherms,

$$\theta = N/N_T \quad (4)$$

where N is the number of sites on the substrate occupied by the anion and is directly proportional to the area of the anion peak and N_T is the total number of sites on the substrate. Consequently, the Langmuir isotherm has two parameters to adjust (K and N_T), and the Frumkin

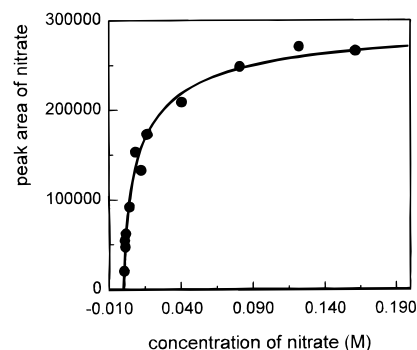


Figure 5. Nitrate peak area as a function of nitrate concentration for Ag/CY. The concentration response is described by the Frumkin isotherm, $\theta = CKe^{2g\theta}/(1 + Ke^{2g\theta})$. Values of g and K for the cationic-coated, silver SERS substrates and nitrate are summarized in Table 1.

Table 1. Summary of the Ion-Pair Constants (K , M^{-1}) and Frumkin Parameters (g) Obtained for the Interaction between the Cationic-Coated, Silver SERS Substrates and Nitrate and Sulfate Ions⁹

cationic coating	nitrate ion	sulfate ion
CY	$K = 350 \pm 50$ $g = -0.33 \pm 0.26$	$K = 1000 \pm 200$ $g = -0.27 \pm 0.23$
CYE	$K = 350 \pm 70$ $g = -0.43 \pm 0.21$	no interaction observed
DMA	$K = 330 \pm 90$ $g = -0.82 \pm 0.96$	$K = 880 \pm 140$ $g = -0.92 \pm 0.22$
DEA	$K = 190 \pm 50$ $g = -0.66 \pm 0.48$	$K = 680 \pm 50$ $g = 0.06 \pm 0.08$
MMP	$K = 1780 \pm 520$ $g = -1.66 \pm 0.51$	spectral interference from MMP

isotherm has three (K , N_T , and g). The concentration profiles were computer analyzed using eqs 2 and 3 and a Marquardt²⁶ nonlinear least-squares fitting routine to obtain the values of K , N_T , and g . As shown in Figure 4, both the Langmuir and Frumkin isotherms adequately describe the low-concentration end. However, only the Frumkin isotherm describes the curved region and higher concentration end of the concentration response (see also Figure 5). Similarly, Crane et al.⁶ demonstrated that the adsorption of Pb^{2+} , Cd^{2+} , and Cu^{2+} with a 4-(2-pyridylazo)-resorcinol coating on a SERS substrate fit a Frumkin isotherm. The non-Langmuir behavior was attributed to the electrostatic repulsions as the metal ions are adsorbed.

The values of the ion-pair constants and Frumkin parameters obtained for nitrate and sulfate and the cationic thiols investigated are summarized in Table 1.⁹ The sign of g indicates the presence of a repulsive or attractive force upon adsorption. In general, for these anions and the cationic coatings investigated, g has a negative value, which indicates that a repulsive force between the adsorbed molecules is present. Initially there is a large electrostatic attraction between the negatively charged anions and the positively charged thiol coating. However, as the surface charge is neutralized by the negatively charged anions, there is a resultant decrease in attraction. The uncertainty in the value of the Frumkin parameter, g , is fairly large. This is attributed to the fact that the Frumkin parameter appears in the exponent. The values of the Frumkin parameters obtained by Crane et al.⁶ and Heynes et al.⁷ in their SERS investigation of metal ion complexation also exhibited fairly large uncertainties.

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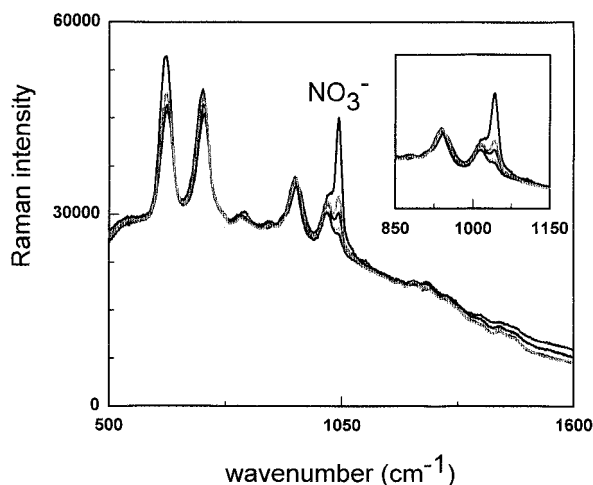


Figure 6. SERS spectra of Ag/CY/nitrate obtained as a function of chloride ion concentration. The concentration of nitrate ion is kept constant at 1000 ppm. The chloride ion concentrations are 0, 5000, 10 000, 20 000, and 30 000 ppm. The insert is an expansion of the nitrate stretching region. The spectra were obtained using 852 nm excitation (laser power is 50 mW at the sample) and 17 s acquisition times.

3.3. Effect of Chloride Ion on the Nitrate Ion Adsorption Isotherm. Figure 6 shows SERS spectra obtained for the Ag/CY/nitrate system as a function of chloride ion. As the chloride ion concentration increases, the intensity of the nitrate ion decreases. As with nitrate and sulfate ions, no enhancement in the SERS spectra of the coating is observed upon exposure to chloride ion. The cationic coatings used in this investigation are very similar to the stationary phases used in ion chromatography. To separate anions, the stationary phases commonly used are comprised of quaternary ammonium groups, $-R_4N^+$, attached to a polymer matrix.²⁷ The stationary phase is generic and interacts with all anions. Retention differences, and consequently the strength of interaction with the stationary phase, are governed by the physical properties of the solvated ions. The stationary phase retains those ions that exhibit a higher charge or a smaller solvated radius or has greater polarizability. It is expected that the cationic coatings used in this investigation will behave similarly to the stationary phases used to separate anions. Therefore, the decrease in intensity of the nitrate ion peak as chloride ion concentration increases is interpreted to indicate that both chloride ion and nitrate ion interact with the cationic coating on the SERS substrate.

Although no new bands for CY occur as a result of interaction with chloride ion, we do observe changes in the spectral peaks due to the C–S stretching modes of the gauche and trans conformers. As chloride ion concentration increases, the intensity of the peak due to the gauche conformer (at 633 cm^{-1}) decreases while the intensity of the peak due to the trans conformer (at 719 cm^{-1}) increases. The intensity ratio of the T band to the G band is indicative of the degree of ordering of the system. The increase in the T/G ratio in the presence of chloride ion indicates that the trans conformation is favored. Of the cationic-coated substrates investigated, only the SERS spectra of CY exhibited any measurable changes in the C–S stretching region upon exposure to chloride ion. It is believed that the flexibility of the other coatings used

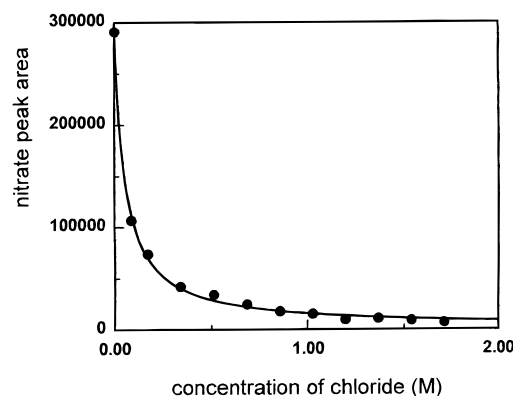


Figure 7. Nitrate peak area plotted as a function of chloride ion concentration for Ag/CY. The spectral data shown in Figure 6 generated this concentration response. The concentration response is described by the following relationship: $\Delta A_{\text{NO}_3} = VC_{\text{Cl}}/(K + C_{\text{Cl}})$. Values of V and K for the cationic-coated, silver SERS substrates investigated are tabulated in Table 3.

Table 2. Pertinent Physicochemical Properties of Chloride, Nitrate, and Sulfate Ions²⁸

property	chloride ion	nitrate ion	sulfate ion
net charge	−1	−1	−2
ionic size (r , pm)	181	179	230
ΔH_{hyd} (kJ mol ^{−1})	−367	−312	−1035
ΔG_{hyd} (kJ mol ^{−1})	−340	−300	−1080

in this investigation is limited by the presence of bulky methyl and ethyl groups. As shown in Figure 3, increasing sulfate ion concentration does not affect the proportionality between the gauche and trans conformers. Carron et al.⁸ reported conformational changes for their octadecylthiol-coated SERS substrates in the presence of benzene. A self-assembled monolayer of octadecylthiol on a silver surface has an all-trans configuration. When benzene partitioned into the coating, they observed changes in the spectrum of the coating consistent with a small amount of gauche conformation.

The response of the nitrate peak area as a function of chloride ion concentration is shown in Figure 7. Chloride does not have any Raman active vibrational modes. Consequently we cannot evaluate the ion-pair constant for chloride directly by monitoring the concentration response of a chloride ion peak. However, we know the magnitude of the ion-pair constant for nitrate ion (Table 1). Since nitrate and chloride are competing for the same sites on the coating, we should be able to extract the value of the ion-pair constant for chloride from the concentration response shown in Figure 7.

3.4. Developing the Model to Describe Competitive Complexation on Cationic-Coated SERS Substrates.

In these experiments, the nitrate ion is kept constant at 1000 ppm and the chloride ion concentration is varied from 0 to 10⁵ ppm. Both nitrate and chloride interact with the cationic coating on the SERS substrate. In developing the model, we will assume that the Frumkin isotherm applies. To adapt the model for two competing species, i and j , we need to assume that the total number of adsorption sites on the SERS substrate is identical for the different species and that $e^{2g\theta}$ is constant. For $e^{2g\theta}$ to be constant requires that the Frumkin parameter, g , be the same for both nitrate and chloride ion and that the total surface coverage, θ , is approximately 1. Table 2 summarizes some pertinent physicochemical properties of

(27) Shugar, G. J.; Dean, J. A. *The Chemist's Ready Reference Handbook*; McGraw-Hill: New York, 1990; pp 4.23–4.28.

chloride and nitrate ions.²⁸ Since chloride and nitrate have identical charge, are of similar size, and have similar solvation properties in water as shown by their free energies of hydration (ΔG_{hyd}), it is expected that the value of g will be approximately the same for both nitrate and chloride. Our experimental conditions (i.e., solution concentrations of nitrate and chloride) are such that $\theta \cong 1$. These assumptions result in the following coupled equations:

$$k_{\text{di}}\theta_i = k_{\text{ai}}C_i e^{2g\theta} (1 - \theta_i - \theta_j) \quad (5)$$

$$k_{\text{dj}}\theta_j = k_{\text{aj}}C_j e^{2g\theta} (1 - \theta_i - \theta_j) \quad (6)$$

where C_i and C_j are the solution concentrations of species i and j ; θ_i and θ_j are the surface coverages of i and j ; and k_{ai} , k_{di} , and k_{aj} , k_{dj} are the rates of adsorption, desorption for i and j , respectively. Solving eq 5 for θ_i and defining $K_i = k_{\text{ai}}/k_{\text{di}}$ gives

$$\theta_i = \frac{K_i C_i e^{2g\theta} (1 - \theta_j)}{1 + K_i C_i e^{2g\theta}} \quad (7)$$

Substituting eq 7 into eq 6, multiplying through by $(1 + K_i C_i e^{2g\theta})$, canceling, and solving for θ_j yields

$$\theta_j = \frac{k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} (1 + K_i C_i e^{2g\theta}) + k_{\text{aj}} C_j} \quad (8)$$

In eq 8, j and i represent the nitrate ion and chloride ion, respectively. The concentration of nitrate is kept fixed, and the chloride ion concentration is varied. We measure the change in the area of the nitrate peak as a function of chloride ion concentration. The relationship between the observed nitrate peak area and the fractional coverage on the substrate is some constant of proportionality, α , and the following is true

$$\Delta A = A_0 - A = \alpha(\theta_0 - \theta) \quad (9)$$

where A_0 and θ_0 are the area of the nitrate peak and the surface coverage of nitrate in the absence of chloride ion, respectively. As the chloride ion concentration increases and interacts with the coated substrate, it displaces the nitrate ion. Consequently, the surface coverage due to nitrate ion decreases, and there is a corresponding decrease in the nitrate peak area. In eq 9, A and θ are the area of nitrate peak and the surface coverage of nitrate in the presence of chloride ion, respectively. The surface coverage of nitrate in the presence of chloride ion is described by eq 8. Substituting eq 8 into eq 9 (and noting by definition that $C_i = 0$ for θ_0) results in

$$\Delta A_j = \alpha \left[\frac{k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}} - \frac{k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} (1 + K_i C_i e^{2g\theta}) + k_{\text{aj}} C_j e^{2g\theta}} \right] \quad (10)$$

rearranging and dividing the numerator and denominator

Table 3. Values of the Parameters that Describe the Change in Nitrate Peak Area as a Function of Chloride Ion Concentration

cationic coating	K (eq 14)	V (eq 14)	correlation (CORRL) ^a
CY	0.053 1 ± 0.002 5	289 800 ± 1600	0.999 21
CYE	0.006 64 ± 0.000 11	100 800 ± 700	0.999 99
DMA	0.037 7 ± 0.004 8	145 300 ± 1800	0.995 69
DEA	0.067 0 ± 0.005 5	175 100 ± 1900	0.997 24
MMP	0.104 ± 0.010	61 600 ± 1000	0.990 49

^a CORRL = $\sum_{i=1}^n w_i^2 (x_i - \bar{x})(y_i - \bar{y}) / [\sum_{i=1}^n w_i^2 (x_i - \bar{x})^2]^{1/2} [\sum_{i=1}^n w_i^2 (y_i - \bar{y})^2]^{1/2}$, where n is the number of points, x is the observed data, y is the calculated value, and w is the weight.

by $(k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}) k_{\text{dj}} K_i e^{2g\theta}$ results in the following expression

$$\Delta A_j = \left[\frac{\alpha k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}} \right] C_i \left\{ \left[\frac{k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} K_i e^{2g\theta}} \right] + C_i \right\} \quad (11)$$

By defining

$$V = \frac{\alpha k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}} \quad (12)$$

$$K = \frac{k_{\text{dj}} + k_{\text{aj}} C_j e^{2g\theta}}{k_{\text{dj}} K_i e^{2g\theta}} \quad (13)$$

we easily see that eq 11 reduces to

$$\Delta A_j = \frac{V C_i}{K + C_i} \quad (14)$$

where $\Delta A_j = A_{0j} - A_j$ (eq 9).

The data shown in Figure 7 were computer analyzed using eq 14 and a Marquardt²⁶ nonlinear least-squares fitting routine to obtain the values of V and K , which are summarized in Table 3 for the cationic coatings evaluated. Table 3 also tabulates the correlation which indicates how well the model fits the data. Since the correlations shown in Table 3 are greater than 0.99, we can conclude that the model describes the data and that the assumptions used to develop the model are valid.

3.5. Evaluating the Ion-Pair Constant between Chloride Ion and the Cationic-Coated SERS Substrates. The ion-pair constant for chloride ion, K_i , is obtained using eq 13 and is given by

$$K_i = \frac{1 + K_j C_j e^{2g\theta}}{K e^{2g\theta}} \quad (15)$$

where K_i , $K_j = k_{\text{aj}}/k_{\text{dj}}$, g , and C_j are the ion-pair constant for chloride, ion-pair constant for nitrate (Table 1), the Frumkin parameter, and nitrate ion solution concentration, respectively. The values for K are tabulated in Table 3. Because eqs 5 and 6 are coupled, it is not possible to experimentally obtain the g values for chloride ion. However, we can either assume no interaction between adsorbed species, i.e., $g = 0$, or we can assume $g_{\text{Cl}} \cong g_{\text{NO}_3}$ and use the g values for nitrate which are tabulated in Table 1. For charge, size, and solvation reasons discussed *vide supra*, it is not unreasonable to expect $g_{\text{Cl}} \cong g_{\text{NO}_3}$. To determine the effect the value of g has on the magnitude of K_i , the values for the chloride ion-pair constants were calculated for $g = 0$ and using the g values for nitrate tabulated in Table 1. The resultant chloride ion-pair

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Table 4. Summary of the Ion-Pair Constants between the Cationic-Coated, Silver SERS Substrates and Chloride Ion Calculated for $g = 0$ and $g_{\text{Cl}} = g_{\text{NO}_3}$

cationic coating	chloride ion-pair constant, K_i (M^{-1})	
	$g = 0$	$g_{\text{Cl}} = g_{\text{NO}_3}$
CY	130 ± 30	140 ± 40
CYE	1000 ± 170	1210 ± 230
DMA	170 ± 40	280 ± 270
DEA	60 ± 10	100 ± 50
MMP	290 ± 80	540 ± 280

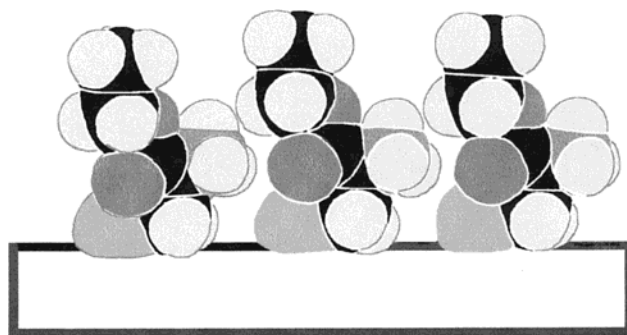
constants are summarized in Table 4. The uncertainties in the chloride ion-pair constants were determined through a propagation of errors treatment.

Comparing the values of K_i for $g = 0$ and K_i for $g_{\text{Cl}} \approx g_{\text{NO}_3}$, we conclude that, within the uncertainties, the numerical values are identical. The uncertainties in K_i obtained using $g_{\text{Cl}} \approx g_{\text{NO}_3}$ are higher because the uncertainties in the values of g_{NO_3} are fairly large, as shown in Table 1. The results summarized in Table 4 indicate that, for both sets of calculations, the ion-pair constant between the chloride ion and the cationic coatings decreases in the order $\text{CYE} > \text{MMP} > \text{DMA} > \text{CY} > \text{DEA}$.

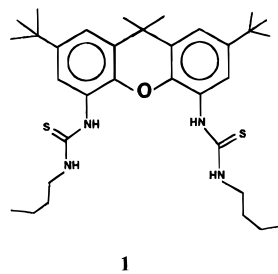
3.6. Selectivity of Cationic-Coated SERS Substrates. As discussed *vide supra*, retention of anions on the stationary phases used in ion chromatography is governed by the physical properties of the solvated ions. The stationary phase comprised of quaternary ammonium groups retains those ions that exhibit a higher charge or a smaller solvated radius or has greater polarizability.²⁶ Nitrate ion is more polarizable than chloride ion and has a lower free energy of hydration (Table 2). Consequently, in chromatographic separations, chloride ion elutes before nitrate, indicating that nitrate interacts more strongly with the stationary phase than chloride. The cationic thiol coatings on the SERS substrates used in these experiments contain a protonated amine group and are very similar to the stationary phases used in ion exchange chromatography. We would, therefore, expect the same principles of ion exchange chromatography to apply to the cationic-coated SERS substrates. In particular, we would expect the interaction of the cationic coatings to be weaker for chloride ion than nitrate ion. As shown by comparing the ion-pair constants tabulated in Tables 1 and 4, except for CYE, nitrate does form stronger ion pairs with the cationic coatings than chloride ion.

For CYE, the strength of interaction with chloride ion is approximately three times stronger than the interaction with nitrate ion. Furthermore, Mosier-Boss and Lieberman⁹ showed that while sulfate ion interacted more strongly with CY, DMA, and DEA, no interaction was observed to occur between sulfate and CYE (Table 1). These results were surprising. In the chromatographic separations described above, sulfate typically elutes after nitrate and chloride, indicating it interacts more strongly with the stationary phase. Although sulfate has a higher free energy of hydration (Table 2) and consequently a larger solvated radius, it does have a larger net charge and is more polarizable than either nitrate and chloride. Therefore, the SERS substrates coated with CY, DMA, and DEA exhibit the expected responses in their interactions with chloride, nitrate, and sulfate ions. For these cationic coatings, the strength of interaction with the anions decreases $\text{SO}_4^{2-} > \text{NO}_3^{2-} > \text{Cl}^-$. But for CYE, the reverse is true which indicates that other factors are involved in the selectivity of this coating.

Xiao et al.^{29,30} reported similar observations for their bis-thiourea ionophore, **1**. In solutions of dimethyl sulfoxide (DMSO), it was shown that the neutral bis-thiourea

**Figure 8.** Computer generated structure of protonated L-cysteine ethyl ester molecules on a silver substrate.

ionophore forms strong complexes with strong hydrogen bond acceptors, such as dihydrogen phosphate, acetate, or chloride, but weak complexes with weak hydrogen bond



acceptors such as hydrogen sulfate, perchlorate, or nitrate.^{31,32} A monolayer of the ionophore on a carbon electrode was selective for the hydrophilic $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$.³⁰ The strength of interaction decreased in the order $\text{HPO}_4^{2-} > \text{F}^- \approx \text{SO}_4^{2-} > \text{CH}_3\text{COO}^- > \text{Cl}^-$. The stability of the interaction with HPO_4^{2-} was attributed to the formation of hydrogen bonds between the oxygen atoms of the anion and the thiourea groups of the receptor. However, incorporating the ionophore in a solvent polymeric membrane resulted in a sensor specific for chloride ion.²⁹ The sensor exhibited reduced interference due to nitrate ion compared to conventional anion-exchanger electrodes. With the exception of sulfate ion, all hydrophilic anions, including $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$, were highly discriminated. The selectivity of the solvent polymeric membrane ISE based on the bis-thiourea ionophore was attributed to the free energies of phase transfer of the anions from the aqueous sample into the organic ISE membrane phase. As a consequence of its lower hydration energy, transfer of chloride from the sample into the membrane phase was energetically more favorable than the phase transfer of phosphate. The results indicated that the selectivity of phosphate binding by the ionophore was not large enough to counterbalance the large difference in the phase-transfer energies of the two ions.

The observations of Xiao et al.^{29,30} may explain the differences in selectivity between CY and CYE for the anions investigated. Figure 8 shows the orientation of CYE molecules on a silver surface. As shown in Figure 8, the protonated amine group of CYE is shielded by the ethyl ester group. To interact with the protonated amine group, the anion has to slip between the ethyl ester groups

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(31) Nishizawa, S.; Bühlmann, P.; Iwao, M.; Umezawa, Y. *Tetrahedron Lett.* **1995**, *36*, 6483–6486.

(32) Bühlmann, P.; Nishizawa, S.; Xiao, K. P.; Umezawa, Y. *Tetrahedron* **1997**, *53*, 1647–1654.

of adjacent CYE molecules. Like the solvent polymeric membrane of Xiao *et al.*'s²⁹ ISEs, the ethyl ester group of the CYE coating is lipophilic. Therefore, to partition between the ethyl ester groups of adjacent molecules to interact with the protonated amine group, the anion has to shed its hydration shell. It is energetically more favorable for nitrate and chloride ions to shed their solvation shells than for sulfate ion. On the basis of solvation considerations, we would have expected the nitrate ion pair with CYE to be stronger than chloride. But our results do not support this expectation and Xiao *et al.*²⁹ saw the same effect with their solvent polymeric membrane ISEs. The results indicate that, when complexing with CYE, the stronger hydrogen-bonding capability of chloride ion negates nitrate ion's greater polarizability and lower free energy of hydration.

4. Conclusions

The interaction of nitrate with cationic-coated silver substrates can be monitored by the SERS response of the nitrate ion. The concentration response is described by the Frumkin isotherm, $\theta = CKe^{2g\theta}/(1 + KCe^{2g\theta})$, which states that the surface coverage of nitrate ion, θ , is determined by the nitrate solution concentration, C ; the ion-pair constant, K ; and the Frumkin parameter, g . Unlike nitrate ion, chloride ion does not have a Raman active vibrational mode. Consequently, the ion-pair constant for the interaction between chloride ion and cationic coatings cannot be determined by directly monitoring the concentration response of a chloride ion peak. Instead, the ion-pair constants for chloride ion can be obtained indirectly using a competitive complexation technique. In this approach, the nitrate ion concentration is kept constant and the chloride ion concentration is varied. The SERS response of the nitrate ion is then monitored as a function of chloride ion concentration. It was found that as the chloride ion concentration increased, the area of the peak due to nitrate decreased. At higher chloride ion concentrations, the response leveled off. These results indicated that both the nitrate and chloride ions were competing for sites on the cationic coating. It was shown

that the change in the nitrate peak area, ΔA_{NO_3} , as a function of chloride ion concentration, C_{Cl} , is described by the following relationship: $\Delta A_{\text{NO}_3} = VC_{\text{Cl}}/(K + C_{\text{Cl}})$. Using the value of K and the value of the ion-pair constant between the cationic coatings and nitrate ion, it was possible to extract the value of the ion-pair constant for chloride ion.

For CY, DMA, and DEA, the strength of interaction with the anions decreases in the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. These cationic coatings interact more strongly with anions that exhibit a higher charge or a smaller solvated radius or has greater polarizability. This is exactly the same behavior observed for the quaternary amine stationary phases used in ion-exchange chromatography. However, CYE does not interact with sulfate ion and interacts more strongly with chloride ion than nitrate ion. Molecular modeling of the Ag/CYE system indicates that the protonated amine group of CYE is shielded by the lipophilic ethyl ester group. To partition between the ethyl ester groups of adjacent CYE molecules to interact with the protonated amine group, the anion has to shed its solvation shell. It is energetically more favorable for nitrate and chloride ions to shed their solvation shells than for sulfate ion. Although nitrate ion is more polarizable and has a lower free energy of hydration than chloride ion, it was observed that chloride formed a stronger ion pair with CYE. The greater strength of interaction between the protonated amine group of CYE and chloride ion is attributed to the stronger hydrogen-bonding capability of chloride ion.

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