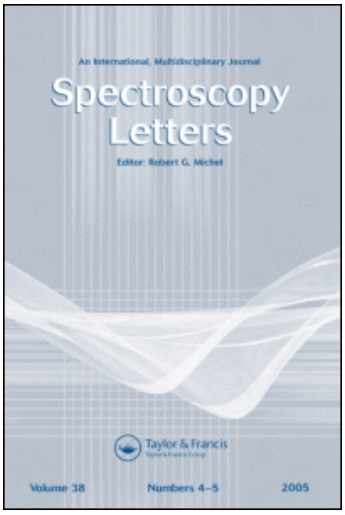

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Adsorption of Cysteamine at Copper Electrodes as Studied by Surface-Enhanced Raman Spectroscopy

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ABSTRACT

The adsorption of cysteamine on a roughened polycrystalline copper electrode in acidic solution has been studied, in-situ, using surface-enhanced Raman spectroscopy (SERS). It was shown that gauche/trans rotational isomerization of the adsorbate depends on the solution concentration of cysteamine. Coadsorption of oxyanions (ClO_4^- and SO_4^{2-}) with cysteamine has been detected spectroscopically. At relatively high cysteamine concentrations (10^{-4} M) the physisorption of oxyanions was evidenced by a minor shift (within 5 cm^{-1}) in the totally symmetric vibrational frequency, as compared with the solution species, and narrow bandwidth (16 cm^{-1}). In contrast, the large downward frequency shift of coadsorbed SO_4^{2-} ions (12 cm^{-1}) and substantial broadening of the band (bandwidth, 29 cm^{-1}) indicated

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chemisorption of the sulfate anions on the copper electrode at low cysteamine concentrations (10^{-7} M).

Key Words: Surface enhanced Raman spectroscopy; SERS; Cysteamine; Copper.

INTRODUCTION

The chemisorption of organic molecules provides a suitable method for modifying the surface properties of metals. Alkanethiols spontaneously form compact two-dimensional films—self assembled monolayers (SAM) on coinage metals.[1–3] Because the physico-chemical properties of the monolayer can be easily modified by variation of the alkyl chain length and the functional terminal group, SAMs have remarkable potential applications in the fields of corrosion inhibition, biotechnology, tribology, and photo-electronic industry.[1,4,5] Recent studies have demonstrated that self-assembled films offer a versatile approach for the protection of copper surfaces against corrosion.[6–8] Especially promising in this field are molecules possessing two surface active groups. Cysteamine ($HSCH_2CH_2NH_2$) is one of the simplest molecules able to bond with the copper surface through its sulfur and nitrogen atoms. A prerequisite for the design of compact monolayers with desirable properties is a fundamental understanding of the forces involved in the self-assembly process, and the characterization of the film at the molecular level.

Surface-enhanced Raman spectroscopy (SERS) is one of the vibrational spectroscopic techniques able to provide in-situ molecular level information on bonding, orientation and conformation of chemisorbed molecules at electrode/electrolyte interfaces.[9–13] SERS has been successfully applied to directly characterize the gauche/trans conformation,[12–18] order within the monolayer,[12,13] as well as interactions of charged terminal groups of the SAMs with solution ions.[16–19] Recently, SERS has been used to investigate the adsorption of cysteamine at silver[15–19] and gold[14,18] electrodes.

In the present work we report the first SERS study on the structure of chemisorbed cysteamine at a copper electrode in acidic solutions.

EXPERIMENTAL

Materials and Instrumentation

Cysteamine was obtained from Aldrich. The Na_2SO_4 and $NaClO_4$ salts were reagent grade, and were recrystalized twice from triply distilled water.

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Electrochemical and SERS measurements were performed in a closed cylindrical three electrode cell. The volume of the spectroelectrochemical cell was 15 ml. The equipment allowed exchange of the cell solution under a controlled potential without removing the electrode from the cell. Prior to use, all the solutions were deoxygenated by bubbling ultra pure Ar through them for 40–60 min. The counter electrode was a Pt wire. Its compartment was separated from the working electrode compartment by a glass frit. The potential of the working electrode was measured vs. an Ag/AgCl, 3M KCl reference electrode (add 208 mV to convert potentials vs. SHE). A polycrystalline Pt disc (0.1 cm^2 geometrical area) inserted in a Teflon rod was used as a working electrode. Before each experiment, the Cu layer was electrodeposited on a Pt surface, as described in the following section. All potentials are given vs. an Ag/AgCl, 3M KCl electrode.

Surface-enhanced Raman spectra were recorded using an f/5.3 double monochromator with 1200 lines/mm gratings equipped with a cooled (approximately 10°C) photomultiplier and a photon counting system. For excitation of the Raman spectra, the 632.8 nm of He–Ne laser beam was incident on the surface at 60° angle and focussed to an approximately 1 mm^2 area spot on the surface with a power of 10 mW at the sample. The laser plasma lines were attenuated by means of an interference filter. Elastic scattering was eliminated with a holographic laser line filter (Kaiser Optical Systems, Inc.) The experiments were performed in 90° geometry. In order to reduce photo/or thermal effects, the spectroelectrochemical cell together with the working electrode were moving with respect to the laser beam ($\sim$20 mm/s).[20] Raman frequencies were calibrated using He–Ne laser plasma lines. The spectral slit width was 8 cm^{-1} in the spectral region of 800 cm^{-1}.

Procedures

The SERS active Cu electrode was prepared as described previously.[21] Briefly, a 10 μm Cu layer was electrodeposited on the Pt surface from an acid copper plating bath (0.5 M $CuSO_4$ + 0.5 M H_2SO_4). Next, an additional Cu layer was electrodeposited from a 0.02 M $CuSO_4$ (pH 4.5) solution at −0.3 V. Electrodeposition time was 120 s. After that the electrode was immersed in deoxygenated 0.5 M H_2SO_4 + 0.5 M Na_2SO_4 solution, and held at open circuit potential for 90 min. Finally, the electrode was rinsed with deoxygenated water and transferred to the spectroelectrochemical cell.

The cysteamine was dissolved in deoxygenated water. Only freshly prepared solutions were used.

RESULTS AND DISCUSSION

Gauche/Trans Isomerization of Adsorbed Cysteamine

Figure 1 compares the Raman spectrum obtained from dissolved cysteamine (1 M) in water with the SER spectrum obtained after the immersion of the activated Cu electrode in 0.1 M $Na_2SO_4 + 0.01$ M H_2SO_4 solution containing 10^{-4} M cysteamine, at -0.100 V. Interpretation of the spectra is presented in Table 1. Isotopic H_2O/D_2O substitution of the solvent was employed in order to discriminate vibrations coupled with the N–H motion (Table 1). First, we will consider the assignments of the solution Raman spectrum of cysteamine. The most intense band in the solution spectrum located at 665 cm^{-1} corresponds to the stretching motion of the C–S bond. The frequency of this mode depends on the gauche/trans

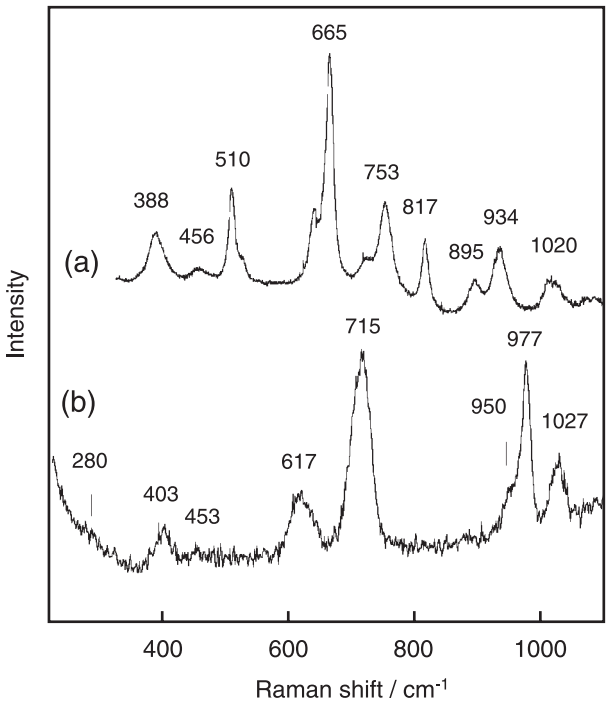

Figure 1. Comparison of the 1M cysteamine solution Raman spectrum (a) with SERS spectrum (b) obtained at -0.100 V from a Cu electrode in 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-4}$ M cysteamine solution.

Table 1. Raman peak frequencies (cm^{-1}) and assignments for cysteamine in solution and adsorbed on copper electrode.

Solution[a]		Adsorbed[b]		
$^{-}SCH_2CH_2NH_3^{+}$				
H_2O	D_2O	H_2O	D_2O	Assignments[c]
–	–	281 w	280 w	ν(Cu–S) ?
388 m	370 m	394[d] w	380[d] w	$\delta(CCN)_G$
–	–	403 m	387 m	$\delta(CCN)_T$
665 vs	661 vs	617 s	620 s	$\nu(C-S)_G$
753 s	734 s	715 vs	700 vs	$\nu(C-S)_T$
934 s	944 m	950 w	–	ν(C–C–N)
1020 m	1001 m	1018[d] m	995[d] w, sh	$\nu(C-C-N)_G$
–	–	1027 m	986 m	$\nu(C-C-N)_T$

Abbreviations: T, trans; G, gauche; vs, very strong; s, strong; m, middle, w, weak; ν, stretching; δ, deformation; ?, assignment unclear.

[a]Raman spectra obtained in 1M cysteamine solution prepared with H_2O or D_2O solvent.

[b]SERS spectra obtained in 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-4}$ M cysteamine solution prepared with H_2O or D_2O solvent at -0.100 V potential.

[c]Assignments based on Refs. [12–19,22].

[d]SERS spectra obtained in 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-7}$ M cysteamine solution prepared with H_2O or D_2O solvent at -0.100 V.

rotational isomerization of the SH and NH_2 groups around the CH_2-CH_2 bond.[22] In the solution phase, gauche conformers dominate and thus the peak at 665 cm^{-1} belongs to the $\nu(C-S)_G$ vibrational mode. The corresponding $\nu(C-S)_T$ peak is located at slightly higher frequency, 753 cm^{-1} (Figure 1a). Particularly interesting is the isotopic sensitivity for the ν(C–S) modes, indicating that the C–S vibrations in cysteamine are substantially coupled with the N–H vibrations (Table 1). Vibrations associated with the stretching motion of C–C–N chain were observed as strong-middle intensity bands at 934 cm^{-1} and 1020 cm^{-1}. Finally, the deformation motion of C–C–N chain in the rotameric gauche isomer in the solution Raman spectrum was identified to be the distinguishable low frequency broad feature located at 388 cm^{-1}.[22] The corresponding mode from the trans conformer was attributed to the 452 cm^{-1} peak observed in the solid state cysteamine Raman spectrum.[22] As can be seen from Figure 1, the SER spectrum completely differs from the solution one, considering both the frequencies and the intensities of the bands. The doublet at 715 cm^{-1}/617

cm^{-1} can undoubtedly be assigned to the vibrations of the C–S bond of adsorbed cysteamine in the trans and gauche conformations respectively.[12–18] Intense ν(C–S) bands were observed earlier for adsorbed alkanethiols at Ag and Au electrodes,[12,13] as well as for the adsorbed cysteamine at Ag[15–19] and Au[14,18] electrodes. Lowering of the ν(C–S) frequency for adsorbed thiols is a result of the withdrawal of electron density at the C–S bond due to the metal–sulfur bonding.[13] It should be noted that a $\nu(C-S)_T/\nu(C-S)_G$ doublet was observed at slightly higher frequencies, 718–728 cm^{-1}/629–647 cm^{-1} and 712–743 cm^{-1}/628–653 cm^{-1} for cysteamine adsorbed at gold and silver electrodes respectively.[18] The decrease in ν(C–S) frequency for cysteamine adsorbed at Cu electrode could be caused by stronger interaction between the sulfur atom and the copper surface as compared with silver and gold substrates. Importantly, the $\nu(C-S)_T$ peak dominates in the SERS spectrum observed at −0.100 V in the 0.1 M Na_2SO_4 + 0.01 M H_2SO_4 solution containing 10^{-4} M cysteamine (Figure 1b), indicating that the main adsorbed species exists in the trans conformational form. We will show later that under certain experimental conditions, it is possible to markedly increase the number of gauche isomers at the interface. In order to facilitate the assignments of the SERS bands, an identical experiment with solution prepared from D_2O instead of H_2O was performed (Figure 2). In this case it was expected to observe a shift in frequency for vibrations coupled with the motion of NH_3^+/NH_2 groups. Indeed, clear shifs of several bands were observed. First of all, the low frequency mode observed at 403 cm^{-1}, in electrolyte prepared with H_2O shifted to 387 cm^{-1} in D_2O solution. Consequently these bands were assigned to the deformation motion of the C–C–N chain, $\delta(CCN)_T$, for the surface bound trans conformer (Table 1). The corresponding bands of gauche conformers were detected in dilute (10^{-7} M) cysteamine solutions at 394 and 380 cm^{-1} prepared with H_2O and D_2O solvent respectively (Table 1). The feature at 1027 cm^{-1} disappeared upon replacing D_2O for H_2O in solution (Figure 2). As can be seen from the difference spectrum, the negative-going band emerged in the D_2O electrolyte at ca. 986 cm^{-1}. The discussed bands fall in the region of the stretching vibration of carbon chains, and were assigned to the $\nu(C-C-N)_T$ vibrational mode (Table 1). The pair of ν(C–S) bands (at 617 and 715 cm^{-1} in H_2O), which corresponded to the vibrations of gauche and trans conformers, showed different sensitivity with respect to H_2O/D_2O exchange. While the intense $\nu(C-S)_T$ peak shifted as much as 15 cm^{-1} (from 715 to 700 cm^{-1}) to lower wavenumbers in D_2O electrolyte, the $\nu(C-S)_G$ component remained essentially unshifted (617 cm^{-1} and 620 cm^{-1} in H_2O and D_2O respectively). A similar tendency was noticed in the solution spectra (Table 1), although, the shift of the $\nu(C-S)_T$ mode was slightly higher (19 cm^{-1}).

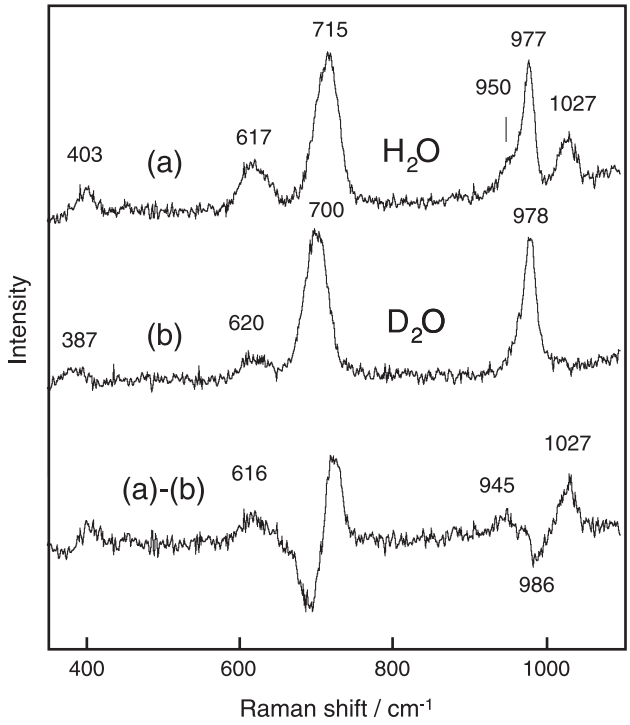

Figure 2. Comparison of the SER spectra obtained from Cu electrode in 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-4}$ M cysteamine solutions prepared with H_2O (a) and D_2O (b). Difference spectrum (a)−(b) is also shown. Electrode potential, −0.100 V. In subtraction procedure spectra were normalized by the intensity of the 977 cm^{-1} peak.

These results indicate that the $\nu(C-S)_G$ mode is uncoupled with the $\nu(C-N)$ and $\delta(N-H)$ vibrations for cysteamine molecules adsorbed at copper electrode, while the coupling of the $\nu(C-S)_T$ mode decreases upon the adsorption. Finally, the prominent feature at 977 cm^{-1} remained unshifted in D_2O solution (Figure 2). The origin of this band will be discussed later.

The intensity of the SER spectra of adsorbed cysteamine on the Cu electrode depends considerably on the potential, and decreases markedly at more negative potential values (Figure 3). The relative intensities of the bands do not change significantly. Although, the slight increase in intensity of the 977 cm^{-1} peak compared with the 715 cm^{-1} peak at a more negative potential (−0.400 V) can be noticed. Such behavior is similar to the observed desorption of n-alkanethiolates at a Ag(111) interface based on

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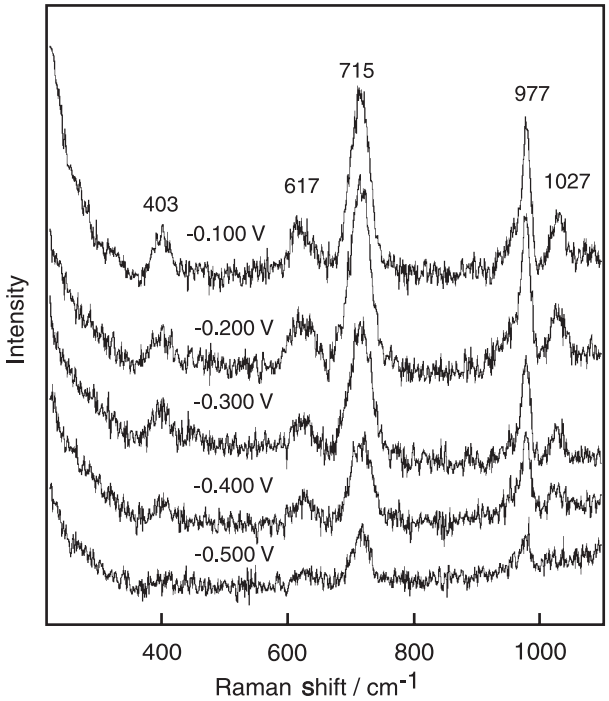

Figure 3. Dependence of SER spectra on Cu electrode potential in 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-4}$ M cysteamine solution.

electrochemical and SERS measurements.[23] It should be noted that at -0.100 V the spectrum was very stable and no significant variation in SERS intensity was observed during six hours.

Contrary to the potential dependence, the concentration of cysteamine in solution dramatically affects the relative intensities in the SERS spectra (Figure 4). At the lowest concentration investigated (1×10^{-7} M) the broad feature at 620 cm^{-1} dominates the spectra. As already discussed, this band belongs to the $\nu(C-S)_G$ vibration of adsorbed cysteamine in the gauche conformation. Thus, it is possible to obtain vibrational SER spectra from adsorbed gauche isomers by applying extremely low concentrations of adsorbate. As can be seen from Figure 4, the frequencies of other vibrational modes of adsorbed gauche rotamers differ considerably from the trans rotamers. First of all, this refers to the stretching motion of the C–C–N chain, the frequency of which shifts to 1018 cm^{-1} for the gauche con-

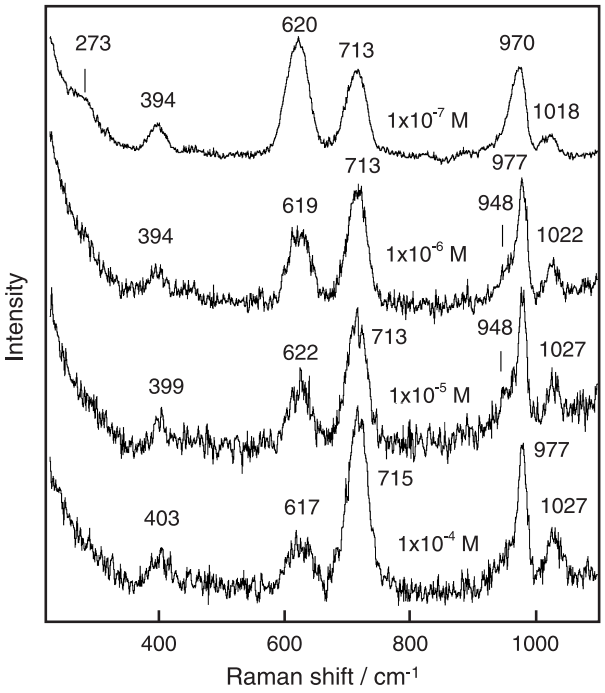

Figure 4. Dependence of the SER spectra on the cysteamine concentration in 0.1 M $Na_2SO_4 + 0.01$ M H_2SO_4 solution at -0.200 V.

former compared to a 1027 cm^{-1} value for the trans conformer (Table 1 and Figure 4). Secondly, the narrow peak at 977 cm^{-1}, in the case of the trans adsorbate, broadens and shifts to 970 cm^{-1} for the gauche isomer. The low frequency deformation vibration of C–C–N chain also decreases in frequency by ~ 9 cm^{-1} and appears at 394 cm^{-1} in the case of adsorbed, predominantly gauche, species (Figure 4). Finally, the broad shoulder at 273 cm^{-1} was observed at low adsorbate concentrations. This peak falls in the frequency range where metal-adsorbate vibrational modes are expected. We tentatively assigned this mode to the Cu–O vibration of adsorbed SO_4^{2-} anions. The presence of sulfate anions at the interface is evidenced by the intense symmetric stretching vibrational band, $\nu_s(SO_4)$, around 970 cm^{-1}.[24,25] Brown and Hope[25] investigated adsorption of sulfate anions on a copper electrode from sulfuric acid solutions by use of SERS. They assigned the low frequency mode at 291 cm^{-1} to the stretching Cu–O vibration of adsorbed SO_4^{2-} ions. An additional complication in the low-

frequency range is associated with the possible influence of the ν(Cu–Cl) band[21] due to the impurities of Cl^- ions in solution, or adsorption of Cl^- ions during the preparation of Cu surface. It should be noted that in the gauche configuration both interaction centers, sulfur and nitrogen atoms, are available for the bonding with the surface,[15–18] while only the sulfur atom is presumably involved in the bonding with the copper surface for adsorbed trans isomers.

As can be seen from the Figure 4, the relative intensity of the $\nu(C-S)_T$ band increases with concentration of cysteamine in solution indicating that the surface coverage ratio of trans/gauche rotamers increases at higher concentrations. This effect can be followed more quantitatively from the dependence of the ratio of integrated intensities A_T/A_G of the $\nu(C-S)_T$ and $\nu(C-S)_G$ bands on the logarithm of cysteamine concentration in solution (Figure 5). Near linear dependence was observed until a concentration of 10^{-4} M. Such dependence in principal could be used for the direct estimation of low cysteamine concentrations in solution. The work in such a direction is in progress in our group.

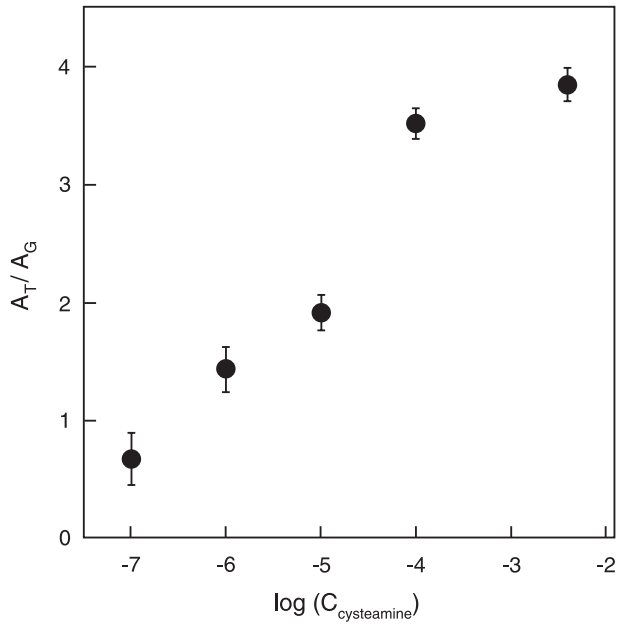

Figure 5. Dependence of the ratio of SER integrated intensities (A) for the $\nu(C-S)_T$ and $\nu(C-S)_G$ modes on the logarithm of the cysteamine concentration in 0.1 M Na_2SO_4 + 0.01 M H_2SO_4 solution at − 0.200 V.

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Coadsorption of Oxyanions with Cysteamine on Cu Electrode

Direct evidence of the coadsorption of oxyanions with cysteamine on the copper electrode is presented in Figure 6. When the SER active copper electrode was immersed in a 0.1 M $NaClO_4$ + 0.01 M $HClO_4$ solution containing 10^{-4} M cysteamine at − 0.100 V, among the other already discussed features a new and narrow band was observed at 933 cm^{-1}. We assigned this band to the totally symmetric stretching vibrational mode $\nu_s(ClO_4)$ of ClO_4^- ion at the interface. In the solution spectra, this mode was observed at 932 cm^{-1}.[25] The narrow bandwidth and absence of a frequency shift are indications that the anion does not directly interact with the surface,[25] but rather forms an ion-pair complex. It should be noted that such an

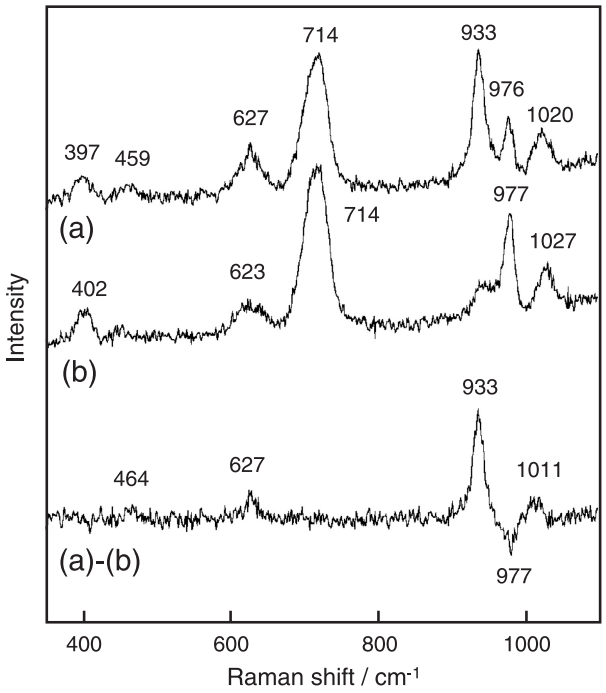

Figure 6. Comparison of the SER spectra obtained from Cu electrode in 0.1 M $NaClO_4$ + 0.01 M $HClO_4$ + 10^{-4} M cysteamine solution (a) and after addition of the 0.01 M Na_2SO_4 (b). Difference spectrum (a)−(b) is also shown. Electrode potential, − 0.100 V. In subtraction procedure spectra were normalized by the intensity of the $\nu(C-S)_T$ mode at 714 cm^{-1}.

interaction is preferred for the adsorbed trans cysteamine isomers. After introduction of Na_2SO_4 solution at -0.100 V until the overall SO_4^{2-}/HSO_4^- concentration reached 0.01 M, the $\nu_s(ClO_4)$ feature completely disappeared and a new narrow band at around 977 cm^{-1} increased in intensity. We assigned this band to the symmetric stretching vibrational mode $\nu_s(SO_4)$ of surface sulfate anion. In the solution spectra this band was observed at 982 cm^{-1}.[25] Such an exchange of oxyanions at an interface is clearly demonstrated in the difference spectrum presented in Figure 6. The positive-going peaks belong to the surface associated ClO_4^- ions, while the negative-going peak at 977 cm^{-1} represents the increased concentration of SO_4^{2-} ions at the interface. The difference spectrum also indicates that the main vibrational bands of adsorbed cysteamine remains unaffected upon exchange of ClO_4^-/SO_4^{2-} ions at the interface. Thus the association of oxyanions with cysteamine at the interface should be weak. It should be noted that the narrow feature at 976 cm^{-1} was observed in perchlorate solutions (Figure 6a). This peak most likely is associated with the SO_4^{2-} ions, coadsorbed during the electrode preparation procedure. The presence of such a band in the spectrum indicates that part of the sulfate anion remains unreplaced in perchlorate solutions. Increased intensities of oxyanions in SER spectra were observed earlier for systems containing irreversibly adsorbed thiourea,[26,27] and cysteamine on silver electrodes.[16,19]

A different state of oxyanions at the interface was observed in dilute (10^{-7} M) cysteamine solutions. Figure 7 compares the SER spectra obtained in perchlorate and sulfate solutions containing a low concentration (10^{-7} M) of cysteamine. The prominent bands at 930 and 970 cm^{-1} can be immediately assigned to the surface-associated ClO_4^- and SO_4^{2-} ions respectively, as they disappear completely in solutions where these anions are absent. Comparison with the SER spectra obtained in concentrated (10^{-4} M) solutions (Figure 6) reveals two important differences. First of all, the frequency of the totally symmetric vibrational mode shifts to lower wavenumbers (from 933 to 930 cm^{-1}, and from 977 cm^{-1} to 970 cm^{-1} for ClO_4^- and SO_4^{2-} ions respectively) as the concentration of cysteamine decreases to 10^{-7} M. Secondly, the bands became considerably broader (for both anions full width at half maximum (FWHM) increases from 16 to 29 cm^{-1}) in the SER spectra recorded in diluted solution. Note that the FWHM value of studied oxyanions in the solution is ca. 8.5 cm^{-1}.[25] These observations indicate that in contrast with the concentrated cysteamine solutions, the anions interact directly with the surface at low cysteamine concentration.[25] The heterogeneity of the surface causes band broadening.[25,28] The difference spectrum of Figure 7 shows that the $\nu(C-S)_G$ frequency of the gauche conformer is sensitive to the nature of the anion in the electrolyte. The peak position of this mode shifts from 627 cm^{-1}, in

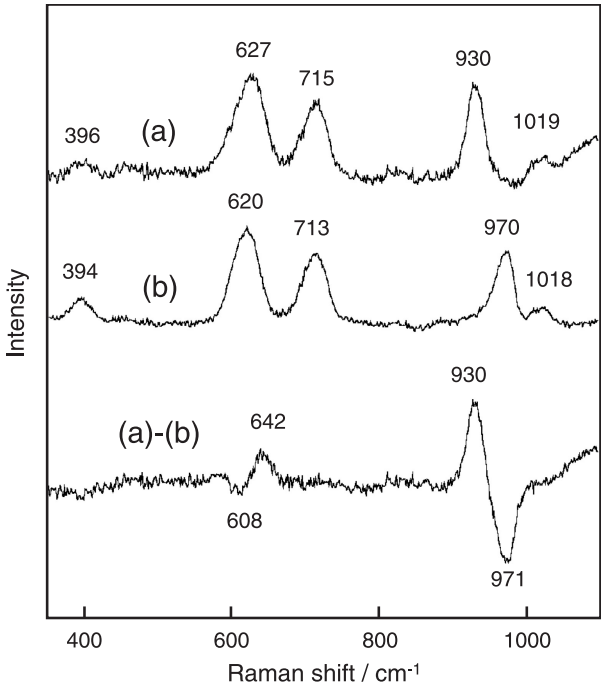

Figure 7. Comparison of the SER spectra obtained from Cu electrode in 0.1 M $NaClO_4 + 0.01$ M $HClO_4 + 10^{-7}$ M cysteamine (a) and 0.1 M $Na_2SO_4 + 0.01$ M $H_2SO_4 + 10^{-7}$ M cysteamine (b) solutions. Difference spectrum (a)–(b) is also shown. Electrode potential, -0.100 V. In subtraction procedure spectra were normalized by the intensity of the $\nu(C-S)_T$ mode at 715 cm^{-1}.

perchlorate, to 620 cm^{-1} in sulfate solutions (Figure 7), but, the $\nu(C-S)_T$ frequency of the trans conformer remains essentially unshifted. The data presented here suggest that the adsorbed cysteamine in the gauche conformation interacts with the surface-bound oxyanions.

Finally, based on the above SERS measurements we would like to present the adlayer model at low and high bulk cysteamine concentrations. At high bulk concentration the adsorbed cysteamine molecules are predominantly in the trans conformation, and interact through the protonated amino groups with oxyanions. The orientation of adsorbed cysteamine is mainly perpendicular to the surface. Most likely formation of ion pairs takes place. Under these conditions oxyanions do not interact directly with the surface. At low bulk concentration the adsorbed cysteamine molecules are predominantly in the gauche conformation and interact through the amino group with chemisorbed

oxyanions. Binding through the nitrogen atom is also possible for gauche conformers, although because solutions with low pH values were used in this study, such an interaction type is less probable.

CONCLUSIONS

Based on a surface-enhanced Raman spectroscopic study we found that by changing the concentration of cysteamine in electrolyte it is possible to control the gauche/trans isomerization of the adsorbate on the Cu electrode surface.

Coadsorption of oxyanions (ClO_4^-) and (SO_4^{2-}) with cysteamine at the Cu electrode surface was observed spectroscopically. It was found that the adsorption state of anions depends on the concentration of cysteamine in solution. At relatively high concentrations (10^{-4} M) the physisorption of oxyanions was evidenced by the minor shift (within 5 cm^{-1}) in the totally symmetric vibrational frequency and narrow bandwidth (FWHM = 16 cm^{-1}). Under these conditions the adsorbed cysteamine molecules are predominantly in the trans conformation and form ion pairs between the protonated amino group and oxyanions. In contrast, the large red frequency shift of coadsorbed SO_4^{2-} ions (12 cm^{-1}), and substantial broadening of the band (FWHM = 29 cm^{-1}) served as an evidence for a chemisorbed state of sulfate anions at low cysteamine concentrations (10^{-7} M). An increase in bandwidth (FWHM = 29 cm^{-1}) was also detected for coadsorbed perchlorate anions under these conditions, indicating a direct interaction of the anions with the Cu surface. The gauche conformation is the predominant state of adsorbed cysteamine molecules at low bulk concentrations. Under these conditions the interaction with chemisorbed oxyanions takes place through the amino group.

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