Study of the Ag$^+$ surface complexes of murexide by SERS and SERRS spectra at Ag electrodes

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Abstract

It is shown that the broadening of the surface-enhanced Raman scattering (SERS) band of murexide adsorbed at Ag electrode in comparison with ordinary Raman scattering (ORS) spectrum is connected mainly with the existence of the two types of well-defined species: molecules adsorbed at active sites and those at ‘normal’ places at electrode surface. The molecules adsorbed at active sites are very similar to the complex of the adsorbate with Ag$^+$ cation. Our observations stress the necessity of the distinguishing of the species present simultaneously at the electrode surface. This is extremely important for the quantitative analysis of resonance Raman (RR) enhancement factor in surface-enhanced resonance Raman scattering (SERRS) experiments because the surface complexes may often exhibit significantly different visible absorption maxima than the ‘free’ molecules themselves. The relative active-site factor of about 4–5 was evaluated from the electromagnetic maximum in the profile of SERS intensity vs. applied potential. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the important enhancement mechanisms in the surface-enhanced Raman scattering (SERS) spectra is the short-distance chemical effect being most frequently considered as a product of photon-driven charge transfer (CT) mechanism and active-sites factor [1]. According to the adatom model proposed by Billmann et al. [2] and Otto [3], the chemisorption of adsorbate occurs at the active sites of metal surface and the SERS signal at electrochemically roughened electrodes is generated mainly by species formed at these active sites. These species can be considered as surface complexes since an adatom resembles Ag$^+$ or Ag$^{+}$ ion [4,5].

The evidence of surface complexes was obtained in numerous SERS experiments on silver electrodes [4–8] and sols [4,9] and has been related to the presence of Ag$^{+}$ ions induced on the metal surface by the coadsorbed Cl$^-$ ions of an electrolyte. However, it was shown that such adatoms are also created during oxidation–reduction cycles (ORC) in the halide anions-free systems and that they are both light and potential sensitive [10,11]. It is worth emphasizing that in most of the studies on adatoms the compounds transparent in visible (VIS) region were...
investigated [5,12,13]. It was observed, for example, that charge transfer excitations between metal and molecule (CT) for pyridine or cyanide ions drastically differ for both species: molecules chemically adsorbed at adatoms and those bound to the metal surface at ‘normal’ places. In some cases, the energy of CT may differ for both such species as much as 0.3–0.8 eV [12,14].

In the present paper, we examine the existence of surface complexes in the murexide (dye)/Ag electrode system. Our purpose was to evaluate quantitatively the active-sites factor in the SERS spectra for this system and then to determine the role of adatoms in the surface-enhanced resonance Raman scattering (SERRS) spectra. The significance of adatoms for the ‘intramolecular’ electronic transition was of our special interest. This study was necessary for further evaluation of electromagnetic (EM) and resonance Raman (RR) contributions to the SERRS spectra of murexide that will be described elsewhere [15].

An additional purpose was to study the influence of pretreatment of Ag electrode on SERS spectra of murexide in terms of active-sites factor and to determine further implications for the analytical applications of SERS.

2. Experimental

The Raman spectra were recorded with a Cary 82 spectrometer equipped with a Spectra Physics Model 165 Ar+ ion laser and a Lexel Model 98 Kr+ ion laser. We used 457.9, 476.5, 488.0, 501.7, 514.5 and 530.9 nm lines of Ar+ laser and 567.8, 647.1 and 676.4 nm lines of Kr+ laser. The spectral bandwidth of spectrometer was set to 4 cm−1. We used the 90° configuration with an angle of incidence on the silver surface in SERS measurements ca. 60°. Typical three-electrode SERS cell was described elsewhere [16]. We used the polycrystalline (99.999% assay) silver electrode as working electrode, 1 M KCl calomel electrode (E = +0.048 V related to saturated calomel electrode (SCE)) as a reference one and a platinum sheet as a counter electrode.

Before spectroscopic measurements the Ag electrode was roughened in a separate cell by an ORC cycle in 0.1 M KCl solution (three cycles from −0.3 to +0.3 V and reverse, sweep rate 5 mV s−1). In the case of non-totally reduced electrode, it was immediately taken out from the electrochemical cell and carefully rinsed with triply distilled water. In the case of reduced electrode, it was kept for 2 min at −0.4 V potential, exposed to neon light (fluorescent tube) for 1 min and rinsed as above. In this procedure, the small amount of AgCl particles remaining after ORC were photoreduced. In the case of deactivated electrode, it was additionally rinsed and kept for 1.5 h at −1.2 V in 0.1 M LiClO4 solution. In the case of modified electrode, the ORC cycles were carried out in the solution containing additionally $2 \times 10^{-3}$ M murexide.

The electrode with an irreversibly adsorbed murexide molecules was obtained by immersion of non-totally reduced electrode for 2 min in aqueous solution of $5 \times 10^{-4}$ M murexide and rinsing carefully 5 times in 0.1 M LiClO4 aqueous solution. Murexide solutions in water are unstable and therefore were prepared directly before measurements.

The SERS measurements were carried out in 0.1 M LiClO4 solution for modified electrode and that with irreversibly adsorbed murexide. In the case of reduced, non-totally reduced, and deactivated electrodes measurements were carried out in $1 \times 10^{-4}$ M murexide solution with 0.1 M LiClO4 as supporting electrolyte.

Murexide–Ag complex (silver purpurate) was prepared by addition of one volume of 0.1 M AgNO3 solution to approximately 20 volumes of $5 \times 10^{-4}$ M murexide red-violet solution. After several minutes from the mixing, a dark violet complex was formed. Molar ratio of metal ions to murexide ions is excessive as compared with the reaction stoichiometry. The obtained complex is chemically stable.

Reagents, i.e., KCl, AgNO3 and murexide, were obtained from Polish Chemical Reagents (POCH) and LiClO4 from Merck, which were of analytical grade. KCl and LiClO4 were crystallized before using. All solutions were prepared from triply distilled water.

3. Results and analysis

Murexide (Ms) is the hydrated ammonium salt of purpuric acid obtained for the first time by Liebig
from urea in the middle of XIX century. Its chemical formula is presented in Fig. 1. In an aqueous solution it has, depending on pH, three forms according to dissociation of acidic imine protons: MsH$_2$ (pH < 9), MsH$^{2-}$ (9 < pH < 11) and Ms$^{3-}$ (pH > 11). Our experiments were carried out in solution at pH = 5 what points out to the first type of anion (Fig. 1).

Ms is commonly used as two-colour indicator in complexometry as strong chelating agent (Fig. 1) [17]. Lately, it was used as proton activity indicator [18]; since 1992 plenty of works on its biologically active derivative—purple acid phosphatase—were done [19]. According to our knowledge, Ms was not investigated by SERS method yet. Relatively weak fluorescence is the main advantage of Ms in comparison to the other widely investigated compounds like rhodamine and cyanine dyes.

3.1. SERS and SERRS spectra at reduced Ag electrodes

Raman, RR, SERS and SERRS spectra of murexide are presented in Fig. 2. As follows from the electronic spectrum of murexide solution presented in Fig. 3, we can use only two lines (647.1 and 676.4 nm) to obtain SERS spectra of murexide. Although VIS absorption spectra of the murexide–Ag complex (Fig. 3) indicate that the preresonance Raman effect might be expected for 647.1 nm laser line, the normalized potential profiles of the spectra obtained with 647.1 and 676.4 nm lines differ only slightly from each other (Fig. 4a,b). It means that for 647.1...
nm, the preresonant Raman effect is negligible and the spectrum for 647.1 nm may be considered as the SERS spectrum.

The band at ca. 720 cm\(^{-1}\) belongs to the most considerably enhanced bands in the SERS spectra together with those at 640–680 cm\(^{-1}\). As follows from the preliminary calculations, the 720 and 640–680 cm\(^{-1}\) bands may be ascribed to skeletal deformations or out-of-plane bending N-H vibrations [15].

In the SERRS spectra, one may also see some other bands, i.e., 1008, 1223, 1293, 1577–1580, 1598–1610 cm\(^{-1}\) (depending on the exciting line) as well as some less intense bands. They are the subject of more detailed analysis [15].

In order to investigate an ‘active-sites’ effect on the SERS and SERRS spectra of murexide, we pretreated the Ag electrodes by four procedures resulting in reduced, non-totally reduced, deactivated, and modified surfaces. The details of pretreatments are described in Section 2.

Fig. 4 shows plots of relative intensity of the 720 cm\(^{-1}\) band vs. applied potential in the SERS spectra recorded with 647.1 and 676.4 nm lines at the reduced Ag electrode.

The broad maximum on the plot of SERS intensity vs. potential cannot be ascribed to the CT effect since there is no potential shift of this maximum with the energy of the laser line. The maximum was
observed in the case of laser lines in resonance (SERRS) [15] (data not presented). It has been suggested [20] that SERRS experiment reflects the changes in a coverage factor and in EM enhancement better than SERS experiment due to much smaller contribution of potential-dependent CT effect in the SERRS spectrum. However, the described maximum is not common for all the bands examined in SERRS experiment, i.e., this maximum does not reproduce exclusively the coverage changes. Hence, the maximum at $-0.35\,\text{V}$ most probably may be ascribed to a reorientation maximum.

Next conclusion may be drawn after analysis of the band shapes in the SERS spectra at the reduced and deactivated electrodes. In Fig. 5, contours of 720 cm$^{-1}$ SERS band at the reduced and deactivated Ag electrodes are shown and compared with the respective bands in RR spectra of $5 \times 10^{-4}$ M solution of murexide and its silver salt. First of all, the intensity of the spectrum for the deactivated electrode is about five times smaller as compared to that of the reduced electrode. Secondly, half bandwidths are also smaller for the deactivated surface (17 cm$^{-1}$ instead of 22 cm$^{-1}$) indicating the possibility of the presence of two components of this band for the reduced electrode (at 718 and 725 cm$^{-1}$, respectively). Similar decrease in half bandwidths was reported in the case of rhodamine 6 G adsorbed on the Ag sol nonactivated by halide ions [9] (in comparison with the activated sol). These components may be clearly seen in the spectrum for the deactivated electrode when the experiment is carried out with 4 cm$^{-1}$ spectral bandwidth, both at $-0.040$ and $-0.340\,\text{V}$ potentials (Fig. 5). As visible in Fig. 5, complexing of murexide by Ag$^+$ ions in solution causes the lowering of the frequency of the discussed band. Thus, we suggest that the 718 cm$^{-1}$ component has to be ascribed to the surface complex of adsorbed molecule with adatoms while the 725 cm$^{-1}$ component arises from the molecules adsorbed at the ‘normal’ places on the electrode surface (not at the active sites). At $-0.040\,\text{V}$, the component ascribed to the complex with adatoms (718 cm$^{-1}$) is dominating while at $-0.120\,\text{V}$ (and at more negative potentials), after partial reduction of adatoms, 725 cm$^{-1}$ band dominates over the lower frequency component. Such two components of CN stretching frequency differing by 21 cm$^{-1}$ were also observed and ascribed to the surface complexes of cyanides adsorbed at two different types of places present at Ag electrode [14].

Note that if we overlapped the two bands at 718 and 725 cm$^{-1}$ with the average halfbandwidth of 15 cm$^{-1}$ corresponding to the solution spectrum (Fig. 5a,f), we might obtain with good accuracy the observed SERS profile.

This is characteristic that in the potential $-0.040\,\text{V}$ at both deactivated and reduced surfaces the frequency of analysed band is equal to 718 cm$^{-1}$.

![Fig. 5. Contours of ca. 720 cm$^{-1}$ SERS band of murexide at different potentials (a–d); excitation line 647.1 nm, Ag electrodes: reduced (---) and deactivated (——) × 5; (a) $-0.040\,\text{V}$, (b) $-0.120\,\text{V}$, (c) $-0.260\,\text{V}$, (d) $-0.340\,\text{V}$. The 720 cm$^{-1}$ Raman band of murexide (e) and silver purpurate (f) from the bulk ($5 \times 10^{-4}$ M solution); excitation line 488 nm.](image-url)
characteristic for complexes. Thus, the conclusion may be drawn that in this potential range the amount of complexes with adatoms is much higher than that at more negative potential values. Moreover, the loss of molecules adsorbed at adatoms at more negative potentials is partially reversible and can be ascribed to the process of desorption mainly from the adatoms due to the decreasing of positive charge at active site centers. Only when working at strongly negative potentials, ca. $-1.2$ V and when using relatively high-energetic blue laser lines both: photo- and potential-driven irreversible loss of adatoms takes place [10,11].

Generally, there is an agreement that a decrease of a lifetime on purely vibrational levels at the metal surface is negligible and the broadening of the SERS bands as compared to the ordinary Raman spectrum (ORS) originates mainly from a great variety of the interactions of adsorbing molecule with the surface [21,22]. Our experiments confirm this opinion.

### 3.2. SERRS spectra at non-totally reduced and reduced electrodes and for irreversibly adsorbed murexide. SERS spectra for modified electrode

In Fig. 6, we present fragments of the SERRS and SERS spectra for several kinds of electrode surfaces pretreated by procedures described in Section 2. One can see that the bands in the SERS spectrum obtained with the electrode roughened in the solution containing murexide (a) and in the SERRS spectra excited with 568.2 nm yellow line, i.e., near the maximum of electronic absorption of the complex (b) exhibit frequency characteristic for murexide–Ag complex. The same frequency was observed in the SERRS spectra at unreduced electrode (c) and for irreversibly adsorbed murexide at reduced electrode (d). As shown above, only at potentials more negative than ca. $-0.120$ V at reduced and non-totally reduced electrodes do the frequency of the observed band is a characteristic for molecules adsorbed at the ‘flat’ surface (725–728 cm$^{-1}$) (Fig. 6e). It is worth mentioning that also when SERS spectra were excited with 676.4 nm line, similar results were obtained. Maximum of the strongest band for reduced electrode at potentials: $E = -0.05$, $-0.35$ and $-0.95$ V appears at 720, 725 and 728 cm$^{-1}$, respectively.

The above seems to be obvious, because in the experiments corresponding to the spectra (a), (b), (c) and (d), we deal mainly with complexes. In the case of modified electrode, we obtain undoubtedly chemical complexes during the roughening pretreatment. At non-totally reduced electrode, the halide ions (remaining at the surface after ORC cycle [3,5]) stabilize the adatoms and therefore the molecules are adsorbed mainly at the active-sites; for irreversibly adsorbed murexide, one might expect more effective adsorption at adatoms than at the other sites at Ag electrode surface [3,5].

Our interpretation finds support in the values of stationary potentials. Table 1 shows the values of an open-circuit (stationary) potential for examined types of electrodes. The values of stationary potentials
Table 1
Values of stationary potentials for various types of Ag electrodes

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>Modified</th>
<th>Unreduced</th>
<th>Irreversibly adsorbed</th>
<th>Reduced</th>
<th>Deactivated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{eq}}$</td>
<td>+0.10 V</td>
<td>+0.05 V</td>
<td>+0.03 V</td>
<td>+0.01 V</td>
<td>−0.02 V</td>
</tr>
</tbody>
</table>

seem to be determined by the (complex/murexide ion, Ag) redox pair, i.e., the higher we expect the surface concentration of complexes, the more positive value of the stationary potential we observe.

Another support for our assumption is obtained from the analysis of a plot of relative SERS intensity of 720 cm$^{-1}$ band vs. applied potential for murexide-modified electrode (Fig. 4c). The maximum observed at $-0.35$ V is relatively smaller when compared with the same maximum for reduced electrode (Fig. 4a). It is obvious when we take into account that in the case of modified electrode, a thick layer of complexes is produced during ORC and then the EM contribution (restricted mainly to the first several layers) enhances SERS spectrum only slightly. Then, the reorientation changes affecting the EM enhancement factor are relatively smaller than in other SERS spectra. Moreover, the decrease in SERS intensity with the decrease of potential is much steeper for modified than for reduced electrode as a proof of reduction process of chemically produced complexes. This observation remains in good agreement with known fact that in situ roughening procedures do not provide surfaces appropriate for analysis of coverage and orientational changes [23].

3.3. Evaluation of active-sites factor in the SERS spectra

Fig. 7 shows the relative SERS intensity vs. applied potential plot for reduced, non-totally reduced and deactivated electrodes. The background of the potential dependence of an intensity of 720 cm$^{-1}$ band (denoted with dash line) is much steeper for reduced electrode than for deactivated one. In the latter case, it is almost flat, parallel to the potential axis. Since no significant morphological changes of 20–100 nm surface roughnesses were found after the deactivation process [21], we may assume that the number of molecules adsorbed at ‘normal’ places does not differ much for reduced and deactivated electrodes. Moreover, we may relate the slope of the background of considered potential dependence with the desorption of murexide anions from the adatoms, since the number of adatoms significantly decreases after the deactivation process and the slope is 8 times less steeper for the deactivated electrode than for the reduced one. The desorption of anionic molecules from the active sites at negative potentials should indeed be expected.

For the non-totally reduced electrode, the slope of a background is steeper than for the reduced electrode indicating, as expected, higher contribution of...
molecules adsorbed at adatoms to the total intensity. Moreover, the intensity of this spectrum is smaller in comparison with reduced electrode. This may be explained in terms of competition between chloride ions and murexide for the adsorption at ‘normal’ places.

Dividing an intensity of the SERS spectrum at 647.1 nm for reduced electrode by intensity of the spectrum for deactivated electrode, we determined the value of an active sites factor. Depending on the potential chosen, we obtained the value of 3.7–5.0. This value is about 2 times smaller than the respective value obtained for pyridine (8) [24]. This difference may be explained by greater chemical affinity of purpurate anion to the flat Ag surface in comparison with pyridine. With increasing the chemical affinity of the adsorbate to the ‘flat’ electrode surface, the adatoms factor is expected to decrease, since relatively more molecules adsorb at the ‘normal’ places on the surface (at concentrations of murexide as high as 10^{-4} M, the adatoms are expected to be saturated [9,25]).

3.4. Comparison of experiments for different types of electrode surfaces

Table 2 shows the SERS and SERRS intensities of 720 cm^{-1} band for all types of electrodes used. One can see that the most intense SERS spectra for 647.1 nm laser line are those for non-totally reduced electrode and for reduced electrode. In the latter case, intensity is slightly smaller probably due to partial loss of adatoms during a preliminary reduction process.

The most striking feature of these data is that the ratio of intensities of the SERRS spectra for non-totally reduced electrode to that for the reduced electrode is about 0.1 for 514.5 nm laser line, while for 647.1 nm laser line (SERS spectra), it is practically equal to 1. It seems that 514.5 nm laser line mainly reproduces changes in the surface concentration of molecules adsorbed at ‘normal’ places (due to strong RR effect of murexide ions), while for 647.1 nm line both: molecules adsorbed at normal places and those at adatoms do not undergo RR enhancement and 647.1 nm line monitors the surface concentration of both kinds of species. Then the above ratios indicate that the number of molecules adsorbed at normal places is much smaller for non-totally reduced electrodes than for the reduced ones. However, in the above analysis, the possibility of different EM enhancement factors for both kinds of species has not been taken into account. It was suggested that the electric field near adatoms may be significantly stronger than that at the flat surface due to the ‘lightening rod effect’. Unfortunately, the respective values of electromagnetic enhancement factors are still not known [26,27].

Strong dependence of the SERS spectra on pretreatment of electrode is well known [28,29]. Analysing the above data one can finally draw the conclusion that direct comparison of quantitative data on relative enhancement factors in experiments carried out at different conditions and on various surfaces is practically impossible and application of the SERS method for analytical purposes meets requirement of rigid reproducibility of experimental conditions. The only surface which practically lacks adatoms is the fully deactivated Ag surface. Unfortunately, SERS spectra for deactivated electrode are much weaker than these for reduced electrode and this diminishes the applicability of this surface for analytical purposes.

Table 2
Comparison of SERS and SERRS intensities [photon counts s^{-1}] of 720 cm^{-1} band of murexide at different types of electrodes

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Modified -0.10 V</th>
<th>Non-totally reduced -0.05 V</th>
<th>Reduced -0.05 V</th>
<th>Deactivated -0.05 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>I_{SERS} 647.1 nm</td>
<td>3268</td>
<td>4641</td>
<td>4487</td>
<td>977</td>
</tr>
<tr>
<td>I_{SERRS} 514.5 nm</td>
<td>n.d.</td>
<td>300</td>
<td>2915</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.d., not determined.

Values are normalized to P = 100 mW and SBW = 5 cm^{-1} for each exciting line. Quantum efficiency of photon counter is not taken into account.
3.5. Excitation profile

After the adatom factor was evaluated in the SERS spectra, the role of adatoms in the SERRS spectra should be investigated. Fig. 3c presents the excitation profile of 720 cm\(^{-1}\) band at \(E = -0.05\) V. It may be seen that surface-enhanced spectrum reaches its maximum intensity at 568.2 nm exciting line which is very near to the maximum of VIS absorption of Ag–murexide anion complex (ca. 570 nm). Analogous dependence exhibiting the maximum at 568.2 nm exciting line was obtained at \(E = -0.35\) V as well (data not presented). Then we may claim that the observed maximum is not due to CT enhancement, but rather to RR enhancement, with maximum of enhancement shifted to the red at the surface when compared with excitation profile for murexide in the solution. The difference in positions of both maxima reaches 0.2 eV.

This seems to be in agreement with so far observations that excitation profile for molecules adsorbed at the surface often differs significantly from that for molecules from solution [30,31]. In the case of murexide, the difference is due to the presence of surface complexes which are similar to the chemical complexes of purpurate ion with Ag\(^{+}\) cations. An analysis of an excitation profile supports our conclusion that at the potential \(E = -0.05\) V, the contribution of complexes with adatoms to the total intensity of both SERS and SERRS spectra at the reduced electrodes predominates the contribution of molecules adsorbed at the ‘flat’ surface. However, as far as we know, the distinction between molecules adsorbed at adatoms and at the ‘normal’ places has not been taken into account in the quantitative evaluation of RR contribution to SERRS spectra.

4. Conclusions

So far, the disability of some SERS theories was that they have not dealt with distinguishing between the molecules adsorbed at active sites and at ‘normal’ places at the surface. Our observations assure the necessity of such distinguishing of the species present simultaneously at the electrode surface. Not only the CT excitations involving Fermi level of the metal may be different for both kinds of species (differing by 0.3–0.8 eV), but also the resonance Raman contributions in the case of VIS-absorbing molecules may be significantly different (for murexide difference in energy of transitions reaches 0.2 eV).

It is shown that the broadening of the SERS band in the case of murexide in comparison with ordinary Raman scattering is connected mainly with the existence of these two types of well-defined species. Active-sites factor has been determined from the reorientation maximum in the profile of SERS intensity vs. applied potential. The value of about 4–5 was obtained.

By changing the pretreatment procedure, one may easily change the ratio of molecules adsorbed at the active sites and at the ‘normal’ ones. This is extremely important for quantitative analysis of the RR enhancement factor in SERRS experiments because surface complexes may often exhibit significantly different VIS absorption maxima than the molecules themselves. It is especially clear for the molecules that create very stable complexes with Ag\(^{+}\) cations. In such a case, the following expression describing the intensity of SERR spectra should be written (compare Eq. 1):

\[
I_{\text{SERRS}} \sim \left[ n_{\text{com}}^x(E) \times G_{\text{RR}}^x(\lambda) \times G_{\text{EM}}^x(E) \right] \\
\times G_{\text{CT}}^x(E) + n_{\text{mol}}^x(E) \times G_{\text{RR}}^x(\lambda) \\
\times G_{\text{EM}}^x(E) \times G_{\text{CT}}^x, 
\]

where all components of the enhancement factors (resonant RR, electromagnetic EM, charge-transfer CT) differ for both kinds of species: molecules adsorbed at ‘normal’ places (mol) and those creating surface complexes with adatoms (com).

However, it still remains unknown if SERRS global phenomenon may be simply ascribed to the combination of EM, CT and RR effects, and if RR and EM contributions to the SERRS spectra are the same as to RR and SERS spectra, respectively.

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References