Electrooxidation of o-methoxyaniline as studied by electrochemical and SERS methods

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Abstract

The electrooxidation of o-methoxyaniline (o-MA) has been studied by electrochemical and surface-enhanced Raman scattering (SERS) methods. The electrochemical measurements showed that the early stages of o-MA electropolymerization were affected by both the monomer to acid concentration ratio and by the acid concentration. The SERS experiments demonstrated the C–N coupling mechanism of o-MA dimerization or oligomerization. The results of both methods indicate that the intermediate redox couple observed in electrochemical response of poly(o-methoxyaniline) can be assigned to the incorporated dimer probably having the cyclic structure.

Keywords: Polyaniline and derivatives; o-Methoxyaniline; Electropolymerization; Electrooxidation; Surface-enhanced Raman scattering

1. Introduction

For the last several years, the electropolymerization of various organic compounds has been investigated with the purpose of obtaining polymer-modified electrodes for specific applications such as sensors, electrochromic materials and catalysts. The morphological, electrical and structural properties of these polymers depend on the synthesis conditions such as the monomer concentration, type of supporting electrolyte, solvent, pH, applied electrical potential and temperature. It was well established that the rate of growth, morphology, density, and redox properties of polyaniline (PANI) are affected by these factors [1–9].

It has been shown recently that poly(o-methoxyaniline) (POMA) has electrochemical properties similar to those of PANI [10–14]. Moreover, POMA can be synthesized chemically and it is more soluble in common organic solvents than PANI [15,16]. Therefore, POMA can be used for manufacturing free-standing films by Langmuir–Blodgett or self-assembling techniques [17].

POMA can also be synthesized electrochemically. However, its electroactivity is influenced by electropolymerization conditions [10–14]. It is an important problem to find the reason for the appearance of the intermediate redox couple and the disappearance of the third redox couple in the electrochemical response of POMA under certain conditions [10,11,13].

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In this paper, we present the effect of the polymerization bath composition (acid concentration, monomer to acid concentration ratio) on the early stages of POMA formation and we look for the origin of the intermediate couple which appears in the electrochemical response of POMA.

2. Experimental

Platinum wire or disc electrodes (99.99% assay, geometric area 0.14 or 0.038 cm²) were used for electrooxidation and polymerization of o-methoxyaniline (o-MA). Current–voltage (i/E) curves were recorded from acidified aqueous solutions (0.2 or 1 M HClO₄) containing varying monomer concentrations. The chemicals (Aldrich) were used as received. A conventional three-electrode one-compartment cell was used in all experiments. Potentials were measured with respect to the saturated calomel electrode (SCE).

The electrochemical setup included an EP 20 programmable potentiostat, an EG 20 generator (both Elpan), an X–Y recorder (BAS), an integrator (Tacussel) and a rotating disc apparatus (Tacussel). Surface-enhanced Raman scattering (SERS) spectra were recorded with a Cary 82 spectrometer using an Ar⁺ ion laser (514 nm) or a Lexel model 98 Kr⁺ ion laser (647.1 nm). The spectra were recorded on a roughened Ag or Au electrode at constant potentials maintained by the potentiostat. The electrodes were roughened by an oxidation–reduction procedure (ORC). The ORC proce-
Table 1
Electrooxidation of o-MA on Pt electrode at v = 5 mV/s

<table>
<thead>
<tr>
<th>c_m (M/dm^3)</th>
<th>M/A</th>
<th>E_p (mV)</th>
<th>i_p (mA/cm^2)</th>
<th>M/A</th>
<th>E_p (mV)</th>
<th>i_p (mA/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.05</td>
<td>693</td>
<td>0.243</td>
<td>0.01</td>
<td>745</td>
<td>0.314</td>
</tr>
<tr>
<td>0.02</td>
<td>0.10</td>
<td>675</td>
<td>0.221</td>
<td>0.02</td>
<td>737</td>
<td>0.457</td>
</tr>
<tr>
<td>0.05</td>
<td>0.25</td>
<td>665</td>
<td>0.400</td>
<td>0.05</td>
<td>725</td>
<td>0.843</td>
</tr>
<tr>
<td>0.075</td>
<td>0.375</td>
<td>645</td>
<td>0.429</td>
<td>0.075</td>
<td>715</td>
<td>1.129</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
<td>708</td>
<td>1.628</td>
</tr>
</tbody>
</table>

* c_m: monomer concentration; M/A: ratio of monomer to acid concentration; E_p: oxidation peak potential; i_p: oxidation peak current.

The procedure consisted of three-fold cycling of the Ag electrode from −0.3 to 0.3 V and back to −0.3 V (sweep rate 5 mV/s) and of cycling the Au electrode 20 times from −0.6 to 1.0 to −0.6 V (sweep rate 50 mV/s) in 0.1 M KCl (o-MA-free solution). The solutions were deoxygenated with argon before measurements.

3. Results and discussion

3.1. Electrooxidation of o-MA

The process of o-MA electrooxidation was studied in 0.2 and 1.0 M HClO_4 solutions containing variable monomer concentrations (10, 20, 50, 75, 100 mM). The oxidation peak potential values (E_p) and peak currents (i_p) of o-MA obtained in the first scan at the sweep rate (v) equal to 5 mV/s are presented in Table 1. An increase in monomer concentration results in a shift of E_p to less positive values and an increase in i_p. However, it is clear that the oxidation potential (E_p) is much higher in 1 M HClO_4 than in 0.2 M HClO_4 with the same monomer concentration. This means that the oxidation potential of o-MA depends on the monomer to acid concentration ratio (M/A). When comparing the i_p values obtained for the same o-MA concentration or the same M/A value it is seen that the peak currents values are higher in more acidic solution, which suggests that the oxidation of o-MA is influenced by both parameters: the M/A ratio and the acid concentration. Similar measurements were carried out with other sweep rates (10, 20, 40 mV/s). As expected, an increase in E_p and i_p values was observed.

3.2. Initial stages of o-MA electropolymorization

It is well known that the electroactivity of PANI or substituted PANIs strongly depends on polymer preparation conditions. We decided to study more systematically the effects of the M/A ratio and of the acid concentration on the initial stages of o-MA electropolymorization. The electropolymorization of o-MA was carried out by cyclic voltammetry in the potential range from 0 to 0.8 V and back to 0 V at a 40 mV/s sweep rate. At least two types of behaviour were distinguished:

(A) characteristic for 1 M HClO_4 solutions with low M/A ratio (below 0.04); Fig. 1(a);

(B) characteristic for solutions with high M/A ratio (above 0.04); Fig. 1(b), (c).

As expected (Fig. 1(a)), the oxidation peak of o-MA at about 0.7 V (the value depends on the M/A ratio and on the acid concentration) and the peak associated with reduction of the oxidized products are seen in the first cycle. The o-MA oxidation current significantly decreases in the initial few cycles giving rise to the currents of two redox pairs: the first (I) with the formal potential (E_f) about 0.17 V and the second (II) with E_f about 0.34 V. In each case, pair II is considerably more pronounced in the i/E curves than pair I, which is observed in the second and following cycles. It was found [11,13] that three redox couples should appear in the i/E curves of POMA. However, the anodic peak potential values (E_{pa} ~ 0.67 V) of couple III lie in the potential range of the o-MA oxidation and this pair is not observed during the electropolymorization at low M/A ratio. When the electrooxidation is prolonged, the o-MA oxidation current begins to increase in subsequent cycles and the oxidation peak potential slightly shifts to less positive values. This effect illustrates the influence of POMA on the monomer oxidation and is more pronounced if the M/A ratio in the polymerization bath is higher. The polymer film obtained by us in 1 M HClO_4 solutions with M/A < 0.04 and measured in the electrolyte in the absence of the monomer showed three redox pairs with a dominating II pair.

The oxidation of o-MA begins at a lower potential and the oxidation peak current (i_p) increases in successive cycles (Fig. 1(b)) in the more acidic solution (1 M HClO_4) at an M/A ratio higher than 0.04. Such a behaviour was observed during polymerization of aniline and was interpreted as the acceleration of the monomer oxidation by polymer film [2,3]. As in case A, only two redox pairs are seen in the i/E curves: I with E_f ~ 0.16 V and II with E_f ~ 0.34 V. However, the ratio of their anodic peak currents (i_{pa}) or cathodic peak currents (i_{pc}) changes depending on M/A; i_{pa}(I) < i_{pa}(II) if M/A < 0.1, i_{pc}(I) < i_{pc}(II) if M/A > 0.1. The polymeric films obtained under such conditions showed three redox pairs in the solution where the monomer was absent.

A different behaviour is observed for 0.2 M HClO_4 solutions with high M/A value. The oxidation peak current decreases in subsequent cycles and E_p shifts to more positive values if the M/A ratio is lower than 0.2. For M/A > 0.2, i_p slightly increases in the initial three cycles and decreases...
thereafter. In both cases, a new anodic peak appears in the $i$/$E$ curves after several cycles (Fig. 1(c)). This peak shifts to less positive values (from 0.7 to 0.64 V depending on the M/A ratio) and its peak current increases with decreasing o-MA oxidation current. Moreover, the cathodic peak current appears at about 0.5 V; it shifts to less positive values and increases in subsequent cycles.

We suppose that this redox pair can be described as the third redox pair of the polymer which appeared in the $i$/$E$ curves at $E_{pa} = 0.65$–0.68 V and $E_{pc} \sim 0.58$ V for 1 M HClO$_4$. It is known that the potentials of this pair are strongly pH dependent [13]. This redox pair is disguised by the oxidation current of the monomer if the proton concentration is much higher than the monomer concentration and it is sufficient to oxidize and protonate the polymer. If the M/A ratio is high then the decrease in proton concentration during the electro-polymerization results in a shift of $E_{pa}$ and $E_{pc}$ of this pair to a potential range where the current of the monomer oxidation is low.

Since the shape of the $i$/$E$ curves can be perturbed by soluble oxidation products we used the RDE (rotating disc electrode) for electropolymerization of o-MA.

3.3. Electropolymerization of o-MA on RDE

Cyclic voltammograms were recorded on a platinum disc electrode at a 1000 rpm rotation speed. The measurements were carried out in 0.2 and 1 M HClO$_4$ solutions containing 20 or 75 mM of the monomer (M/A ratio 0.1, 0.02, 0.375, 0.075) in the potential range from −0.2 or 0 to 0.8 V and back to −0.2 or 0 V at a 40 mV/s sweep rate. After polymerization, the RDE was removed, carefully washed in acid
solution (0.2 or 1 M HClO₄, respectively) and measured at stationary conditions in the solution without monomer. The \( i/E \) curves recorded on a rotating electrode during the electropolymerization showed that the shape of the curves depended on the M/A ratio and on the acid concentration.

The oxidation current of \( \alpha \)-MA decreased in successive cycles in the solutions with low monomer concentration. However, the second redox pair clearly seen in the second cycle under stationary conditions (see Fig. 1(a)) appeared after about 1 h in 1 M HClO₄ when the M/A ratio was equal to 0.02 and after 10 min in 0.2 M HClO₄ with M/A ratio equal to 0.1. The redox pair I appeared only as a shoulder on the \( i/E \) curves. As can be seen in Fig. 2(a), one electroactive product is formed during the electropolymerization (polymerization bath 20 mM \( \alpha \)-MA, 1 M HClO₄). The \( E_r \) of this redox pair is equal to 0.348 V, the \( E_{pa} \) and \( E_{pc} \) values are independent of \( v \) in the 40–160 mV/s range; \( E_{pa} - E_{pc} = 0.045 \) V. The dependences of \( i_{pa} \) and \( i_{pc} \) on \( v \) are linear, indicating that the electroactive product is surface-attached.

We believe that the \( \alpha \)-MA dimer is formed as a dominant product in these cases (M/A = 0.02 in 1 M HClO₄ and M/A = 0.1 in 0.2 M HClO₄) during the initial stages of polymerization. The \( E_r \) value is very close to the formal potential of the linear head-to-tail aniline dimer, \( p \)-aminodiphenylamine (ADPA) [18]. However, the \( E_r \) value of the product formed during the early stages of \( \alpha \)-MA electropolymerization is also close to the redox potential of phenoxazines like oxonine or Nile Blue A measured in 1 M H₂SO₄ [19]. Therefore, the product cannot be unequivocally identified with the linear head-to-tail \( \alpha \)-MA dimer.

An increase in the oxidation current of \( \alpha \)-MA in successive cycles was observed and the oxidation started at a lower potential in each cycle when the electropolymerization was carried out in the bath containing 75 mM monomer in 1 M HClO₄ solution (M/A = 0.075) as in the stationary electrode measurements. Two redox pairs (I and II) were seen as early as in the fifth cycle and the pair III (\( E_{pa} \approx 0.62 \) V) appeared in the \( i/E \) curves after about 15 min. The \( i/E \) curves obtained for such an electrode in 1 M HClO₄ under stationary conditions are presented in Fig. 2(b). Three redox pairs are clearly seen in the \( i/E \) curves. The I and III pairs can be assigned to poly(\( \alpha \)-MA). The first anodic process can be related to the oxidation of leucoemeraldine to the protonated emeraldine form of POMA and the third anodic process corresponds to the oxidation of emeraldine to the perigraniline structure. We suppose that the second redox pair can be assigned to the residual \( \alpha \)-MA dimer or to the cyclization products formed by polymerization. Different behaviour was observed when the polymerization bath contained 75 mM of \( \alpha \)-MA in 0.2 M HClO₄ (M/A = 0.375). The oxidation current of \( \alpha \)-MA decreased during the initial few cycles and then started to increase. Two well-defined redox pairs (I, III) were observed in the \( i/E \) curves (Fig. 3(a)) after about 20 min. When the polymerization was prolonged to about 30 min, the anodic and cathodic currents of both pairs increased and the \( E_{pa} \) and \( E_{pc} \) of the pair III shifted to less positive potential values. This effect illustrates the effect of depletion of protons during the polymerization on the redox properties of the polymer. When such an electrode was immersed in acid solutions (Fig. 3(b)) the redox properties of poly(\( \alpha \)-MA) were restored.

The electrochemical measurements showed that both stages of \( \alpha \)-MA polymerization and the redox properties of POMA were affected by the M/A ratio and by acid concentration. However, we used the SERS method to determine possible products formed by \( \alpha \)-MA oxidation.

3.4. SERS spectra of \( \alpha \)-MA on Au and Ag electrodes

We have recorded the SERS spectra of a rough Au electrode immersed in acidified \( \alpha \)-MA solutions (0.02 and 0.1 M) in order to identify the species that formed at the electrode
Fig. 3. (a) Cyclic voltammograms obtained during electrooxidation of 75 mM \textit{o}-MA + 0.2 M HClO\(_4\), M/A = 0.375, on RDE with 1000 rpm and at sweep rate 40 mV/s, after 20 min (---) and after another 20 min (-----). (b) Cyclic voltammograms of FOMA (formed under the conditions in Fig 3(a)) in 0.2 M HClO\(_4\) (---) and 1 M HClO\(_4\) (-----) at sweep rate 40 mV/s.

surface during \textit{o}-MA electropolymerization. In the case of the Au surface, the SERS experiments are feasible with the red laser light only; therefore, similar experiments were carried out with the Ag electrode using green (514.5 nm) and red (647.1 nm) lines to excite the SERS spectra. Let us discuss these experiments first as they have allowed us to interpret the SERS results for Au electrode correctly.

The SERS spectra of a 100 mM \textit{o}-MA solution in 0.2 M HClO\(_4\) at the Ag electrode, recorded with the 514.5 and 647.1 nm lines for two electrode potentials, −0.2 and +0.2 V, are presented in Fig. 4. The spectra recorded with the 514.5 nm excitation are rather poor, exhibiting several weak bands at 760, 830, 1370, 1450, 1500 cm\(^{-1}\) and a strong band at 1590 cm\(^{-1}\) which can be assigned to the adsorbed \textit{o}-MA (Table 2). The spectrum intensity increases at positive potentials but no new bands appear. A totally different picture is observed with the 647.1 nm excitation. The SERS spectrum at negative potentials is extremely weak, some new bands (585, 1170, 1265, 1335, 1378, 1535, 1590 cm\(^{-1}\) are the strongest) appear at 0 V (not shown here). The spectrum reaches the intensity maximum at +0.4 V and reversibly decreases after the potential has been scanned to its negative end. It can be deduced from the comparison of the spectra observed with 514.5 and 647.1 nm excitation lines that new species are formed at the electrode surface at positive potentials; they absorb light of wavelengths about 647.1 nm, resulting in the resonance Raman effect. Thus, the spectra excited with 647.1 nm line are in fact the surface-enhanced resonance Raman (SERRS) spectra rather than ordinary SERS spectra detected when the 514.5 nm line has been used. The bands seen in the SERRS spectra (Fig. 4(b)) can be assigned to the products of \textit{o}-MA oxidation at the electrode surface.

Quite similar SERRS spectra were observed for acidic \textit{o}-MA solution (100 mM) at the Au electrode surface (Fig. 5). A rather weak spectrum resembling that observed for the Ag electrode with 647.1 nm excitation is readily detected at negative electrode potentials. As it can be concluded from the experiments carried out with the Ag electrode, the main bands at 585, 1170, 1270, 1335, 1375, 1530 and 1595 cm\(^{-1}\) are doubtless due to \textit{o}-anisidine oxidation products. These products can be formed at the electrode surface even at the open-circuit potential. Shifting the electrode potential to more positive values results in a considerable increase in the SERRS intensity, which reaches its maximum at +0.4 V. This intensity increase can be assigned to an increasing amount of oxidation products close to the electrode surface. The total intensity of the spectrum diminishes on returning to negative potentials.

As seen from Fig. 5, there are some changes in the relative intensities of the SERRS bands with the electrode potential. The 1335 and 1375 cm\(^{-1}\) bands are almost equal in intensity at negative potential values, while the lower frequency band (1335 cm\(^{-1}\)) becomes more intense at positive potentials. The bands in this frequency region are the key bands of semiquinone radical cations and they have been assigned to the C–N=C symmetric stretching vibrations of the species having the C–N bond order intermediate between single C–N and double C=N [20,21]. A similar doublet (1338 and 1342 cm\(^{-1}\)) was detected by Gao et al. [22] in the SERS spectrum of \textit{N}-phenyl-1,4-phenylenediamine irreversibly adsorbed on the Au surface, which was subjected to electrooxidation. As reported by Harada et al. [21], the \textit{N,N'}-diphenyl-1,4-benzenediamine radical cation (BBB') has also two bands, 1383 and 1401 cm\(^{-1}\), in the resonance Raman spectrum excited with the red laser line (632.8 nm). On the other hand, two bands of lower frequencies (1344 and 1320 cm\(^{-1}\)) were detected [21] in the spectrum of polymerized PANI. The same doublet was observed in the Raman spectrum at the Pt electrode recorded during polymerization of 0.1 M aniline in acid medium [23] and was assigned to the
Fig. 4. SERS (a) and SERRS (b) spectra of 100 mM o-MA solution in 0.2 M HClO₄ at Ag electrode: (a) λₑₓ = 514.5 nm; (b) λₑₓ = 647.1 nm. Electrode potentials: (———) and (− × −) −0.2 V; (———) and (− · −) +0.2 V.

Table 2
Raman frequencies observed for liquid o-MA and their assignments

<table>
<thead>
<tr>
<th>Liquid o-MA</th>
<th>Assignment [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>515 m</td>
<td>vₒ₂, δ(C=O) B₂</td>
</tr>
<tr>
<td>585 vw</td>
<td>v₆₁, δ(CC) A₁</td>
</tr>
<tr>
<td>760 vs</td>
<td>v₁₁, ring A₁</td>
</tr>
<tr>
<td>843 m</td>
<td>v₁₂, C=O</td>
</tr>
<tr>
<td>1026 m</td>
<td>v₁₃, δ(C=C) A₁</td>
</tr>
<tr>
<td>1044 s</td>
<td>δ(CC) CH₃</td>
</tr>
<tr>
<td>1158 m</td>
<td>v₉₈, δ(CH) A₁</td>
</tr>
<tr>
<td>1185 m</td>
<td>v₁(O=CH₃)</td>
</tr>
<tr>
<td>1227 vw</td>
<td>v₁₅</td>
</tr>
<tr>
<td>1278 m</td>
<td>v₇₆, v(CC) A₁</td>
</tr>
<tr>
<td>1342 m</td>
<td>v₄₄, v(C=O) A₁</td>
</tr>
<tr>
<td>1460 w</td>
<td>v₁₃₄, v(CC) B₂</td>
</tr>
<tr>
<td>1509 w</td>
<td>v₁₃₉, v(CC)</td>
</tr>
<tr>
<td>1598 m</td>
<td>v₉₉, v(C=O) A₁</td>
</tr>
<tr>
<td>1620 m</td>
<td>v₁₆</td>
</tr>
</tbody>
</table>

*a: very weak; w: weak; m: medium; s: strong; vs: very strong.

linear dimer produced by the 'head-to-tail' coupling of the monomer. Thus, we may conclude that the dimeric (or oligomeric) species formed during o-MA electrooxidation in acid solution are mainly the products of the C–N coupling of the monomers. This conclusion has been supported by other spectral changes seen in Fig. 5. A new band at 1485 cm⁻¹ is detected at potentials starting from +0.2 V. It is most intense at +0.4 V and disappears at negative potentials. This band can be unequivocally assigned to the C=N band of the oxidized (quinone diimine) form of oligomeric species at the electrode surface [20,21].

A similar series of SERRS spectra was recorded for more dilute (0.02 M) acid (0.2 M HClO₄) o-MA solution during the electopolymerization process (Fig. 6). The bottom spectrum (at 0 V) can be essentially assigned to monomeric o-MA molecules adsorbed at the electrode surface (see Table 2). However, some bands (1325, 1535 and 1640 cm⁻¹) can hardly be assigned to the monomer. Switching the electrode potential to +0.7 V results in considerable changes in the spectrum. The frequencies and in some cases the relative intensities of the previously detected bands change, the bands at 1570, 1440 and 1150 cm⁻¹ assigned to the o-MA monomer disappear and some new components (at about 1490, about 1210 and 1135 cm⁻¹) appear in the spectrum. A significant increase in the SERRS scattering and the appearance of two new 1175 and 1340 cm⁻¹ bands were observed after applying a negative potential (−0.1 V). After this experiment, the electrode surface was covered with a thin blue deposited film. The SERRS spectra were recorded again after the electrode had been removed from the solution and carefully rinsed with distilled water. Then, the electrode surface was in contact with 0.2 M HClO₄ solution which did not contain o-MA. These spectra are presented in Fig. 7. The SERRS spectra recorded during the last experiment (Fig. 7) are almost identical with the spectra recorded during the o-MA electrooxidation (Fig. 6). Thus, the Au electrode was covered with the thin film of electrooxidation and/or electropolymerization products after the potential had been increased to +0.7 V and the spectra observed at −0.1 and +0.4 V are in fact the SERRS spectra of this film. The spectra shown in Fig. 7 are essentially very similar to the ex situ Raman spectrum of protonated POMA salts excited with the 632.8 nm line [24]. However, it is impossible to compare our data because the spectrum range reported in [24] was limited to 1100–1700 cm⁻¹. There are some differences between the SERRS spectra recorded with the dilute (0.02 M) o-MA solution (Figs. 6 and 7) and the corresponding spectra at the Au electrode recorded for a concentrated (0.1 M) solution (Fig. 5). They are as follows:
Fig. 5. SERRS spectra of 100 mM o-MA solution in 0.2 M HClO₄ at Au electrode at λₜ₁ = 647.1 nm. Electrode potentials: (—) −0.2 V; (— —) +0.4 V; (− × −) +0.1 V; (− ⊘ −) −0.3 V.

Fig. 6. SERS (at 0 V) and SERRS spectra of 20 mM o-MA solution in 0.2 M HClO₄ at Au electrode at λₜ₁ = 647.1 nm. Electrode potentials: (—) 0 V; ( — — ) +0.7 V; (− × −) −0.1 V.

(i) several bands are visible (800, 840, 1135, 1210 and 1645 cm⁻¹) for the 0.02 M solution which are not detectable for the 0.1 M solution;

(ii) the 1485 cm⁻¹ band assigned to the ν(C=N) vibration of quinone diimine units [20,21] disappears at negative potentials in the case of 0.1 M solution, while it remains quite strong for the 0.02 M solution;

(iii) the overall intensity of the SERRS spectrum is highest at positive potentials for 0.1 M solution, while the strongest spectrum is detected at negative potential values for 0.02 M solution.

The above facts can suggest that at least two different electrooxidation (electropolymerization) products are formed at the electrode surface and their relative amounts depend on the monomer concentration. The very high intensity of the SERRS spectrum at −0.1 V (Fig. 7) in the case of more dilute solution indicates that some new species giving strong resonance Raman or surface-enhanced resonance Raman spectra are formed at negative potentials along the linear oligomeric units which predominate in the case of the 0.1 M o-MA solution. We suppose that these species are possibly the cyclization products resulting from the process similar to that suggested for o-aminophenol [25]. The structure of such a cyclic dimer is very similar to that of oxazine-type dyes (e.g. oxazine 1, Nile Blue, etc.). As follows from the literature data [26], these dyes exhibit electronic absorp-
tion in the red part of the spectrum. Thus, the bands at frequencies close to 1640, 1210, 1140 and about 840 cm⁻¹, which appear in the spectra shown in Figs. 6 and 7, can be assigned to the oxazine-type structure [27].

The 585 cm⁻¹ band, very strong in the spectrum at −0.1 V, is also characteristic for the oxazine-type dyes. For example, this band assigned to the ring deformation vibration is the strongest in the resonance Raman spectrum of Nile Blue [26]. A very strong, resonantly enhanced band at 585 cm⁻¹ was also observed in the SERS spectrum of phenazine at the Ag electrode [28].

The same band appears in the SERRS spectra recorded for 0.1 M o-MA solution (Fig. 5) but it should be pointed out that its intensity in the last spectrum (at −0.1 V) of the series reproduced in Fig. 5 is about 0.5 of that of the phenyl ring vibration band at 1600 cm⁻¹ and about unity in the corresponding spectrum presented in Figs. 6 and 7. It means that some other species which absorb the red laser line contribute to the SERRS spectrum in the case of the 0.02 M o-MA solution. We suppose that these can be oxazine-like cyclic o-MA dimers.

4. Conclusions

In our opinion, the electrochemical results indicate that the intermediate couple (pair II) cannot be assigned to the deg-