Charge transfer processes on electrodes modified by polymer films of metal complexes with Schiff bases

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ABSTRACT

Electrochemical properties of glassy carbon electrodes modified by two polymer films of different nickel complexes with Schiff base ligands containing methoxy substituents in their aromatic parts were studied in acetonitrile solutions with cyclic voltammetry, quartz crystal microbalance, atomic force microscopy, and impedance spectroscopy. It was observed that introduction of such substituents leads to a noticeable splitting of cycling voltammetric curves into at least two ox/red transitions. In addition, solvent flows accompanying the counter-ions ones during charging/discharge processes within the films appeared significantly greater than those observed in the case of non-substituted ligands. The obtained impedance results as a whole were satisfactorily treated in scope of the so-called model of homogeneous films with two kinds of charge carriers. However, determinations of the Warburg constant as a function of the electrode potential require additional verifications, at least in the ranges of overlapping ox/red transitions. In particular, it was established that in this region the impedance frequency dependence was some superposition of the diffusion (Warburg) and the pseudo-capacitive constituents. This, most likely, resulted from the presence of three kinds of charge carriers in the film interior.

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1. Introduction

Polymeric complexes of transition metals with Schiff bases have been the source of much interest during last 20 years. This interest is mainly due to a variety of potential applications of electroactive polymers, including their use in chemical and biological sensors, electrocatalytic systems, molecular electronic devices, advanced batteries, and ultracapacitors [1,2].

Schiff bases are compounds containing the azomethine group (RC=N—) and are usually formed via condensation of a primary amine with an active carbonyl compound. They act as tetradentate ligands and form complexes with different transition and non-transition metals including copper, cobalt, nickel, palladium, platinum, and others. Some of the most extensively used Schiff bases are salicylaldehyde-based ligands, especially SalEn (N,N′-ethylene-bis(salicylidenimine)) and its derivatives. The general formula of a [M(Schiff)] complex is shown in Fig. 1.

Some of [M(Schiff)] complexes can be polymerized oxidatively at an electrode surface in weak donor solvents to form thin electroactive polymeric films. At present, more than 50 poly-[M(Schiff)] compounds have been prepared. Despite intensive investigation over two decades, the mechanism of polymerization remains a matter of controversy. Goldsby [3] suggested that polymerization took place through the formation of C—C bonds between the monomers at *para*-positions of the phenyl moieties. The proposed mechanism of polymerization was a ligand-based process, in which radical-radical coupling between phenyl rings took place. However Shagisultanova and co-workers [4] and later Peters and co-workers [5] proposed a metal-based process, in which the metal is first oxidized as Ni(II) → Ni(III) + e−, after which the oxidized species could form a charge-transfer stabilized stacked deposit. Peters et al. [5] suggest that this process is followed by a second electron transfer, which involves 2 electrons and results in C—C bond formation, giving rise to a more compact film.

The electrochemical activity of the polymers is also a matter of debate: Timonov [4] and Peters [5] suggested that the redox wave observed was metal based, while Audebert [6] and later Freire [7] proposed that it was ligand based, after observing that

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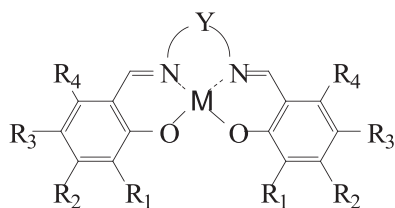[1] ISE member.

Fig. 1. General formula of [M(Schiff)] complexes based on salicylaldehyde. Y is a "bridge" group, R_1–R_4, substitutes in the aromatic part of a ligand. Schiff = SalEn at R_1–R_4 = H and Y = CH_2—CH_2.

the metal had an insignificant effect on the conductivity of the film. In the last two decades various groups were investigating these compounds using voltammetry and chronoamperometry [8,9], in situ spectroelectrochemical methods such as UV–vis spectroscopy and FTIR spectroscopy [9,10], in situ ellipsometry [10], and electrochemical quartz microbalance [9,11,12]. Some years ago we have performed the study of poly-[Ni(SaltmEn)] complex (M = Ni, Y = C(CH$_3$)$_2$—C(CH$_3$)$_2$, R_1–R_4 = H, Fig. 1) using impedance spectroscopy [13]. In the course of that study, it has been established that cyclic voltammetric (CV) curves of the corresponding modified electrodes possess a couple of sufficiently broad peaks, which are complicated with pronouncedly expressed shoulders. This observation allowed one to assume the existence of two redox transitions in the polymer films under discussion, although the only one electron transfer process of Ni(II) – e ↔ Ni(III) might be expected in such systems. At the same time, the obtained impedance data did not reveal any intriguing and unexpected findings related to the above complicated character of CV-curves. This work continues that investigation; now we have chosen two very stable polymers, which seem promising for practical applications: poly-[Ni(CH$_3$O-SaltmEn)] – M = Ni, Y = C(CH$_3$)$_2$—C(CH$_3$)$_2$, R_1 = OCH$_3$ R_2–R_4 = H and

poly-[Ni(CH$_3$O-SalPhen)] – M = Ni, Y = ⬡, R_1 = OCH$_3$ R_2–R_4 = H (Fig. 1). The main difference of such polymers as compared to those studied previously is the presence of the methoxy substituents in aromatic parts of Schiff base ligands of precursor monomer complexes. We will therefore use terms "non-substituted" and "substituted" ligands at the subsequent comparison between the corresponding results.

2. Experimental

Initial complexes were synthesized using standard procedure [14]. Polymer films were formed in a potentiostatic mode on a polished glassy carbon disk electrode of 0.07 cm^2 area. To synthesize the films, we prepared solutions, containing 0.001 M monomer and 0.1 M Et$_4$NBF$_4$ in acetonitrile, and applied the electrode potential of 1 V. Thickness of the film was controlled by the charge consumed for electrodeposition. According to the calculations described in Ref. [13], the condition of polymerization for obtaining poly(Ni(CH$_3$O-SalPhen)) film of 1 μm thickness is 4 mC charge, for 2 μm thick film – 7 mC. Poly(Ni(CH$_3$O-SaltmEn)) films of 1 μm and 2 μm thickness were polymerized by applying of 4.5 mC and 10 mC of electricity to the electrode, correspondingly. Acetonitrile of extra pure grade (VECTON, Russia) and other reactants of reagent grade (Aldrich) were used. All measurements were performed in a hermetically sealed three electrode cell at 25° C. To remove dissolved oxygen, solutions were bubbled with nitrogen of extra purity grade (99.999%, Lentekhgaz). Electrochemical measurements (cyclic voltammetry (CVA) and impedance spectroscopy) were carried out in 0.1 M Et$_4$NBF$_4$ acetonitrile solutions in a cell consisting of a working electrode, counter electrode – platinum plate, and a reference electrode (Ag wire in a 0.1 M AgNO$_3$

solution in AN). However, for consistency all the potentials are quoted vs. aqueous Ag/AgCl (KCl sat.) reference electrode.

The utilized equipment included an Autolab PGSTAT30 (Eco Chemie, Netherlands) and Epsilon 2 (BAS, USA). Prior to the tests, freshly synthesized films were cycled in the potential range 0–1 V during at least 20 cycles (at sweeping rate v = 50 mV/s) until stable electrochemical response was achieved. To check the electroactivity of the films, cyclic voltammograms (CVs) were recorded before and after the relevant measurements. Only if the recorded currents differed from each other no more than 10%, the obtained results were then processed.

EQCM measurements were performed with QCM 100 Quartz Crystal Microbalance Analog Controller and QCM25 Crystal Oscillator (SRS, USA). The area of Pt working electrode was 1.37 cm^2. A morphological study of the polymers was carried out using an atomic force microscope P47 ("NT-MDT", Zelenograd, Russia). Image processing was performed applying computer program NOVA-1138.

3. Results and discussion

3.1. Cyclic voltammetry (CV) and microbalance (EQCM) measurements

As illustrated in Fig. 2a and b, in cyclic curves of electrodes modified with polymer films of two different complexes
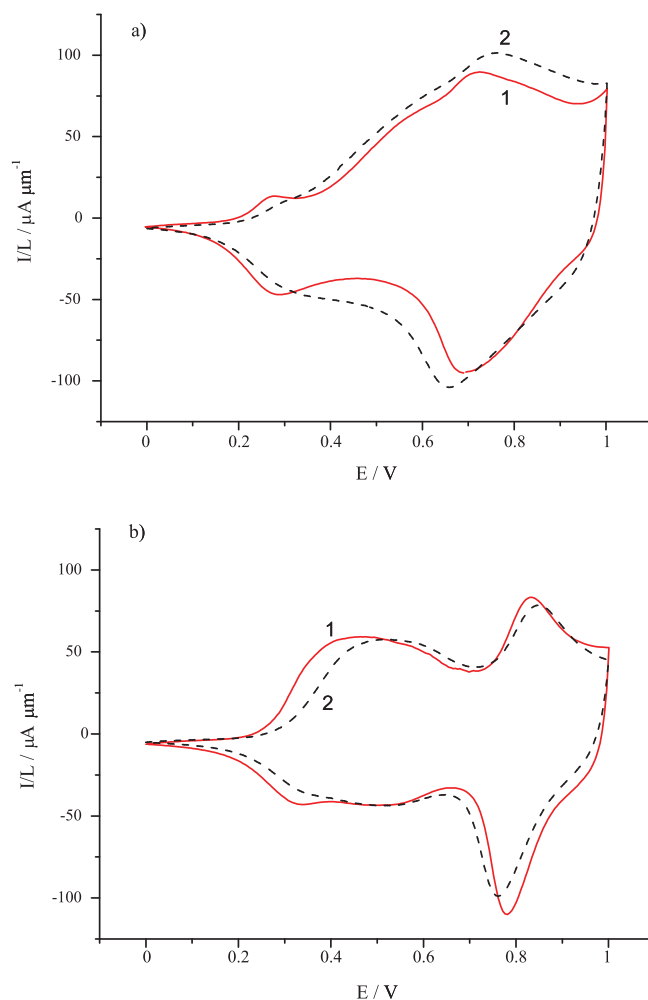

Fig. 2. Cyclic voltammograms of polymer films of 1 μm (curve 1) and 2 μm (curve 2) thickness. Current values are normalized on the film thickness; scanning rates are 50 mV/s. (a) Poly-[Ni(CH$_3$O-SalPhen)] film. (b) Poly-[Ni(CH$_3$O-SaltmEn)] film.
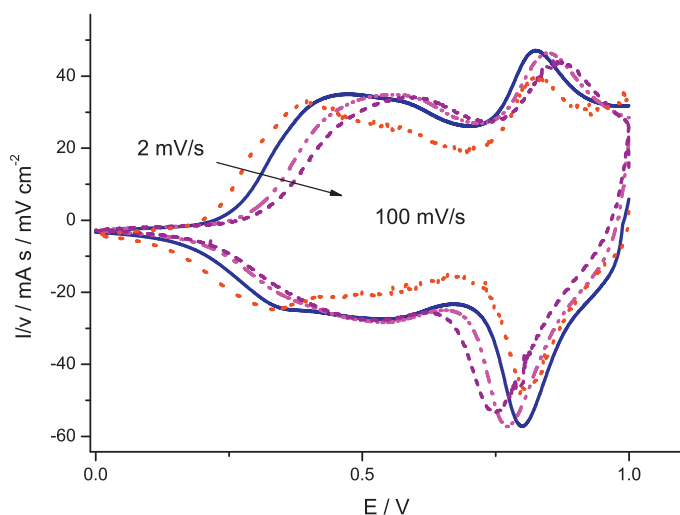
Fig. 3. Cyclic voltammograms of 2 μm thick poly-[Ni(CH₃O-SaltmEn)] films. Current values are normalized by scanning rate values. Data for scanning rates equal to 2–100 mV/s are represented.

Ni(CH₃O-SalPhen) and Ni(CH₃O-SaltmEn), one can observe at the minimum two sets of relatively broad peaks. It can also be seen, that in both cases, the reduced currents (i.e. the ratios of I/L, where L, the film thickness) recorded for two different values of L (approximately equal to 1 and 2 μm) at scan rate $\nu = 50$ mV/s differ insignificantly from each other. This allows to assume quasi-monolayer occupancy of both films with their ox- and red-fragments in the course of recording CV-curves, i.e. the practical absence of charge carriers' gradients within the film interior. To confirm the validity of such assumption for films of Ni(CH₃O-SaltmEn), we studied the dependence of their CV-curves on scanning rate ν. As one could expect based on the above results, the currents normalized on the scanning rate (i.e. values of I/ν) appeared to be weakly dependent on ν (see Fig. 3), which confirmed the above assumption. At the same time, as seen from Fig. 3, the peaks of the observed charge transfer transitions shift upwards in the electrode potential values with the increase in the scanning rate, especially in case of the first transition (in the range of 0.3–0.6 V). This most likely indicates some slowness of one or two steps of charge carrier's injection into the film volume. Analogous results (but in a less pronounced form) were observed for films formed from Ni(CH₃OSalPhen) complexes. Thus, one can assume that, in the conditions of CV-recordings, charge transfer processes in the films under consideration are hardly limited with diffusion of charge carriers, but partially controlled by the injection steps.

Here, it is necessary to emphasize an essential difference of the above results from those obtained in case of non-substituted ligands [13]. If, in the last case, CV peaks were complicated only with some shoulders indicating the presence of additional redox transitions, the CV-curves of electrodes modified with methoxy substituted polymer complexes at the minimum show the existence of two well-defined redox transitions (see Fig. 2a and b). Besides, as was established in Ref. [13], the peak currents of electrodes covered with non-substituted polymer complexes were proportional to scanning rate ν only at small values (up to $\nu = 30$ mV/s), while, in the limit of its high values ($\nu \geq 100$ mV/s), these currents were proportional to the square rooted scan rate. Thus, in contrast to the films of complexes with substituted ligands, diffusion of charge carriers is most probably a limiting step of charge transfer within the films formed from non-substituted complexes at the conditions indicated.

In connection with the observed existence of at least two redox transitions in CV-curves of the modified electrodes under

discussion, one more question arises. Namely, what concrete causes are responsible for the appearance of these transitions? To answer this question, it is first necessary to establish some stoichiometric relations characterizing charge transfer within the studied films. In this context, we indicate that number n of electrons consumed for reduction/oxidation of one polymer repeat unit of the studied film can be determined in result of parallel CV and EQCM measurements by using the following relation [12]:

$$n = \frac{QM}{Fm} \tag{1}$$

Here, Q is the amount of electricity consumed on complete reduction/oxidation of a polymer film in the supporting electrolyte solution not containing species capable to reduce/oxidize on the modified electrode studied; m, the mass of a dried polymer film in its neutral state; M, the molar mass of a single polymer fragment ($M = 441$ g/mol and $M = 433$ g/mol for Ni(CH₃O-SaltmEn)- and Ni(CH₃O-SalPhen)-complexes, respectively) and F, the Faraday number. It has been established that number n turns out equal to 1.0 ± 0.1 for both kinds of poly-[Ni(Schiff)] films, which is in agreement with the results obtained earlier for poly-[Ni(SalEn)] films using thin-layer voltammetry [5]. Therefore it is reasonable to assume that one electron transfer: poly-[Ni(II)-Schiff]⁰ − e ↔ poly-[Ni(III)-Schiff]⁺¹ accompanies processes of the polymer fragment's oxidation/reduction. If so, exactly one anion of unitary charge per one transferred electron is required to maintain electroneutrality of the films as macroscopic objects. To determine the molar mass of species entering/leaving the film at its discharge/charging, the results of corresponding EQCM measurements were treated by using relation, which has, in essence, the same form, as that given in Eq. (1). In particular, replacing quantities M and Q/m in Eq. (1) by the molar mass of transferred species (M) and derivative dQ/dm (where $m(Q)$, the film mass change followed from the Sauerbrey equation [15]), conformably, and taking into account the determined value of $n \approx 1$, one has the well-known equation;

$$M = \left(\frac{1}{F}\right)\frac{dQ}{dm} \tag{2}$$

As it is seen from Table 1, the determined molar masses of transferred species exceed by 1.5–2 times (depending on the polymer studied) the mass of anions BF₄⁻¹ (87 g/mol) of salt Et₄NBF₄, 1 M acetonitrile solutions of which were used at corresponding measurements. In our opinion, excessive masses of transferred species (as compared to that of BF₄⁻¹-anions) should be assigned to the existence of solvent (AN) flows conjugated with anion ones that accompany charging/discharge processes in question. If so, the number of solvent molecules per one transferred anion appears approximately equal to 3 and 4 in cases of poly-[Ni(CH₃O-SaltmEn)] and poly-[Ni(CH₃O-SalPhen)] films, correspondingly. Analogous data obtained for polymer complexes not containing methoxy groups in the aromatic parts of the ligands are also represented in Table 1 (see the second and forth rows of the table), since a comparison between such results and those indicated above seems useful. As follows from such a comparison, transition to the non-substituted ligands leads to a noticeable decrease in the numbers of

Table 1
Molar mass and composition of particles, participating in oxidation/reduction of poly-[M(Schiff)].

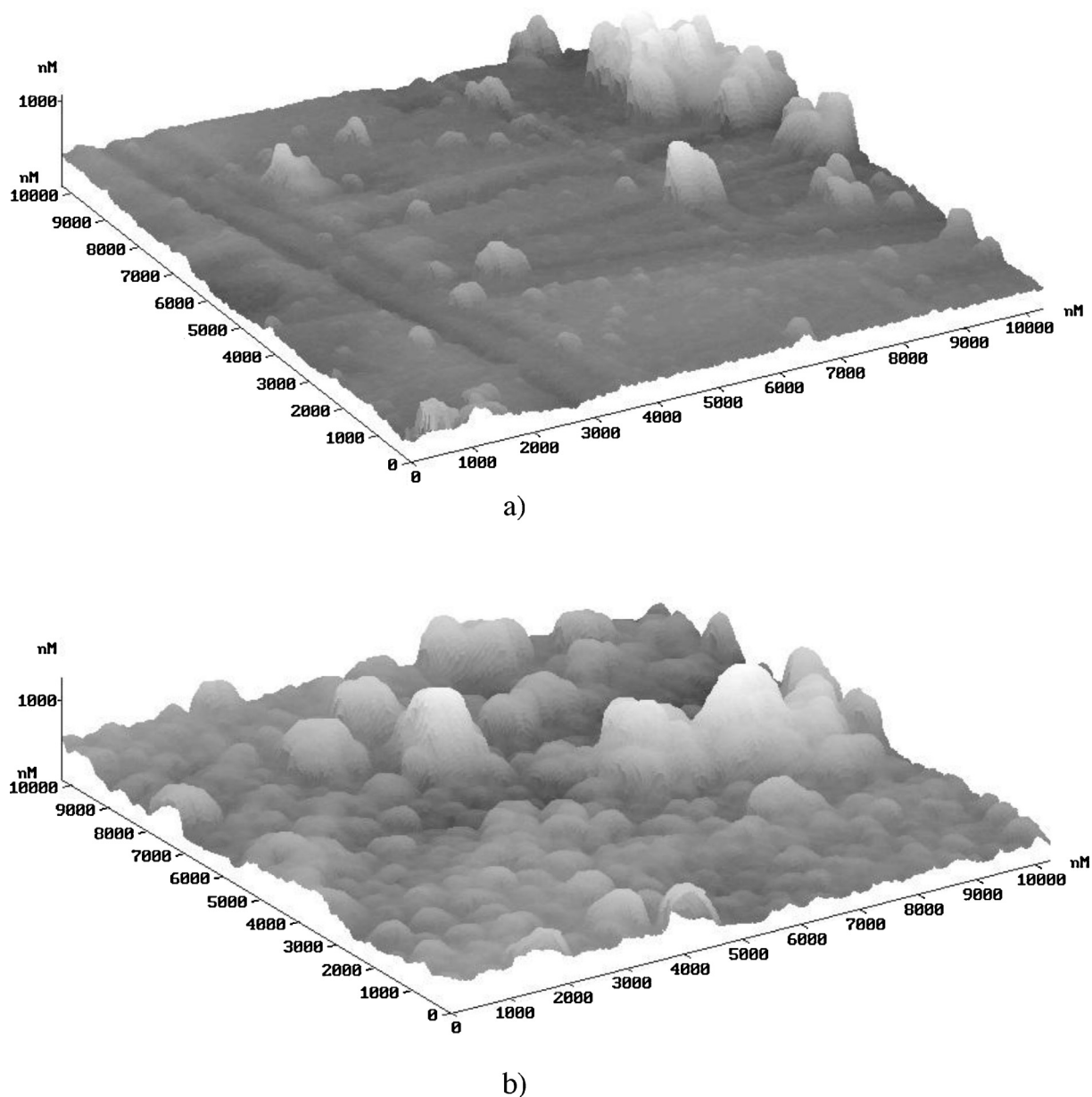| Polymer	Molar mass and composition of charge transfer agents, participating in oxidation/reduction, g/mol	
Poly-[Ni(SaltmEn)]	130 ± 5	BF₄⁻ + AN
Poly-[Ni(CH₃O-SaltmEn)]	220 ± 5	BF₄⁻ + 3 AN
Poly-[Ni(SalPhen)]	150 ± 10	BF₄⁻ + 1.5 AN
Poly-[Ni(CH₃O-SalPhen)]	260 ± 10	BF₄⁻ + 4 AN

a)

b)

Fig. 4. AFM-pictures of 1 μm polymer films. (a) Poly-[Ni(SalPhen)] and (b) poly-[Ni-o-(CH₃O-SalPhen)].

transferred solvent molecules up to 1.5–1, thus the resultant molar mass becomes close to the molar anion one. These data allow one to think about significant changes in the solvent content of the polymer films formed from complexes with non-substituted and methoxy-substituted ligands. In any case, the performed introduction of the methoxy group in the ligand environment of the initial complexes also causes changes in the morphology of the studied films. Namely, it leads to the increase in the diameter of polymeric globules by two times at the average (from 100 to 180 nm), as it can be seen from Fig. 4.

If the above one-electron character of redox transitions is accepted, at first sight, it is difficult to explain the appearance of two (or even more) transitions separated sufficiently in electrode potentials, at least in case of poly-[Ni(CH₃O-SaltmEn)] films. To explain these transitions seems possible if one assumes the existence of three kinds of charge carriers within the film interior instead of two ones usually considered. As to the nature of such charge carriers, it is still discussed. As was mentioned above, in the literature three models are presented, the first of which describes

the polymers in question as typical conjugated ones with polaronic and bipolaronic conductivity [6,7]. The second model states that poly[M(Schiff)]-films are stacked supramolecular structures with metal-based conductivity [4,5], the third model is a combination of the previous ones [1,10]. The appearance of two redox transitions in scope of each model was discussed in our previous paper [16].

3.2. Impedance measurements

Impedance spectra of electrodes modified with 1 μm films of substituted SalPhen- and SaltmEn-complexes of Ni are represented as the Nyquist plots in Figs. 5 and 6, correspondingly. These spectra do not change their shapes significantly at the transition to thicker films ($L \approx 2$ μm), so we will further discuss only 1 μm thick films. Both types of plots are characterized by the absence of high frequency semicircles (at least at frequencies lower than 100 kHz), demonstrating the Warburg and subsequent pseudo-capacitive increases of the imaginary ($-Z''$) and real (Z') impedance constituents with decreasing angular frequency $\omega = 2\pi f$
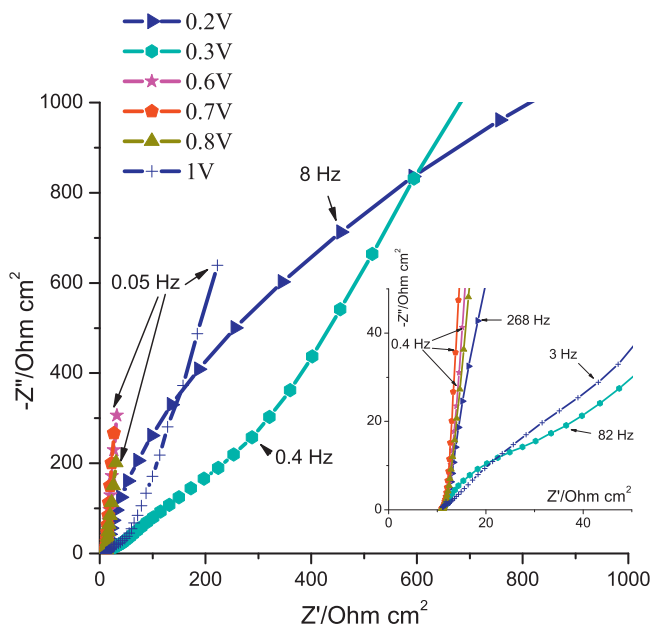
Fig. 5. Impedance spectra of 1 μm thick poly-[Ni(CH$_3$O-SaltmEn)] film. Potentials of spectra registrations are indicated on the graph.
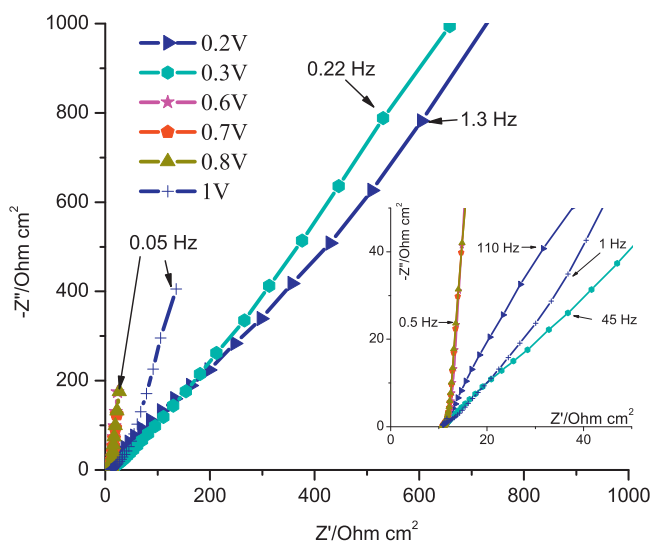

Fig. 6. Impedance spectra of 1 μm thick poly-[Ni(CH$_3$O-SalPhen)] film. Potentials of spectra registrations are indicated on the graph.

(10^5 Hz $\leq f \leq 10^{-1}$ Hz) of the applied alternating potential of small amplitude equal to 10 mV. Here, it could be added that such plots do not qualitatively differ from those obtained previously for non-substituted polymer complexes of [Ni(SaltmEn)] [13]. Some exception from such behavior is observed only at potentials corresponding to the edges of the redox activity range of polymers (about 200–300 mV and 1 V for both complexes). In particular, one can see from Figs. 5 and 6 that a tendency of forming a loop is observed in the Nyquist plots at these potentials. Taking into account the above mentioned shifts of CV-curves with increasing scan velocity, which are observed at the same potentials, it is reasonable to treat such loops as indications of a partial control of charge transfer by injection steps at these conditions. At ac frequencies below 1 kHz and potentials exceeding peak ones (300–400 and 1000 mV), linear dependences of $-Z''(Z')$ with the slope close to $\pi/4$ are observed in the corresponding plots (see curves 0.3 V, 1 V in Figs. 5 and 6), i.e. the Warburg constituent of the impedance is explicitly revealed.

Thus, the obtained data of impedance measurements appear to be non-trivial most likely resulting from several redox transitions, the existence of which complicates obviously a desirable treatment of these data.

The impedance theory is so well elaborated in the case of films containing two kinds of charge carriers [17–19], that it provides a semi-quantitative description of proper experimental results [20]. At the same time, we must underline here that one can expect such a correspondence only if the studied system in its main features satisfies the model assumptions accepted in the scope of this theory. As to the systems in question, they do not satisfy these model assumptions due to the presence of several redox transitions, the potential regions of which overlap each other. In other words, an adequate description of these systems might be achieved only if the existence of three kinds of charge carriers in the film interior is taken into account, as was mentioned above. The impedance theory of such systems is absent. We will therefore apply the existing theory assuming it to be valid approximately, at least in case of poly-[Ni(CH$_3$O-SaltmEn)] film modified electrodes, the peak potentials of which are relatively far apart. In such conditions, the theory should be valid for the beginning of the first redox transition and the end of the second one, at least, since contributions of these processes to the measured currents are small in the corresponding regions of CV-curves. Besides, we also took into account the fact that the existing theory adequately described the impedance results obtained previously for non-substituted complexes [Ni(SaltmEn)], in case of which the existence of three kinds of charge carriers seemed also reasonable [13].

We will further use some simplified equations from work [18] by Mathias and Haas. Restricting ourselves to the case of insignificant diffusion impedance in the supporting electrolyte solution (since no influence of stirring the solution on experimental results was observed), we will represent impedance $Z(\omega)$ within a middle frequency range as follows

$$Z(\omega) = Z'(\infty) + \frac{RT(t_e^2 + t_m^2)((1 + a_0\theta(1-\theta))/C\theta(1-\theta) + 1/z_x^2 c_x)}{F^2 A (j\omega D_{ef})^{1/2}} \quad (3)$$

In this equation, $Z'(\infty)$ is the value of the Warburg impedance extrapolated at $f = \infty$; t_e and t_m, the transference numbers of electrons and counter-ions (here, BF_4^{-1}-anions); c_x, the concentration of counter-ions in the bulk film; z_x, their charge (here, $z_x = -1$); C, the total concentration of redox sites; θ and $(1-\theta)$ are the fractions of oxidized and reduced sites, correspondingly; a_0, the so-called attraction constant characterizing short-range interactions between film fragments; D_{ef}, the effective diffusion coefficient of charge carriers inside the polymer film; A, the electrode area; $j = \sqrt{-1}$, is the imaginary unit; other notations have their usual meaning.

At low frequencies the corresponding expression for impedance Z_{LF} has the following form:

$$Z_{LF} = Z'(\infty) + L^2 \frac{1 - 3t_e t_m}{3D_{ef}C_{LF}} + \frac{1}{j\omega C_{LF}} \quad (4)$$

where low-frequency capacity C_{LF} of the film is given by the equation.

$$C_{LF} = \frac{F^2 AL}{RT((1 + a_0\theta(1-\theta))/C\theta(1-\theta) + 1/z_x^2 c_x)} \quad (5)$$

Here, it is convenient to start from the results obtained for low-frequency capacity C_{LF} of the studied films. According to Eq. (4), capacity C_{LF} can be calculated from slope $d(-Z'')/d(\omega^{-1})$ of the $Z''(\omega^{-1})$-dependence in the indicated frequency region. Such dependencies for both electrodes modified with films under consideration are represented in Fig. 7a and b for different values of potentials (see legend to the figure). From these plots one can see that, as it is required by Eq. (4), a reverse proportionality between
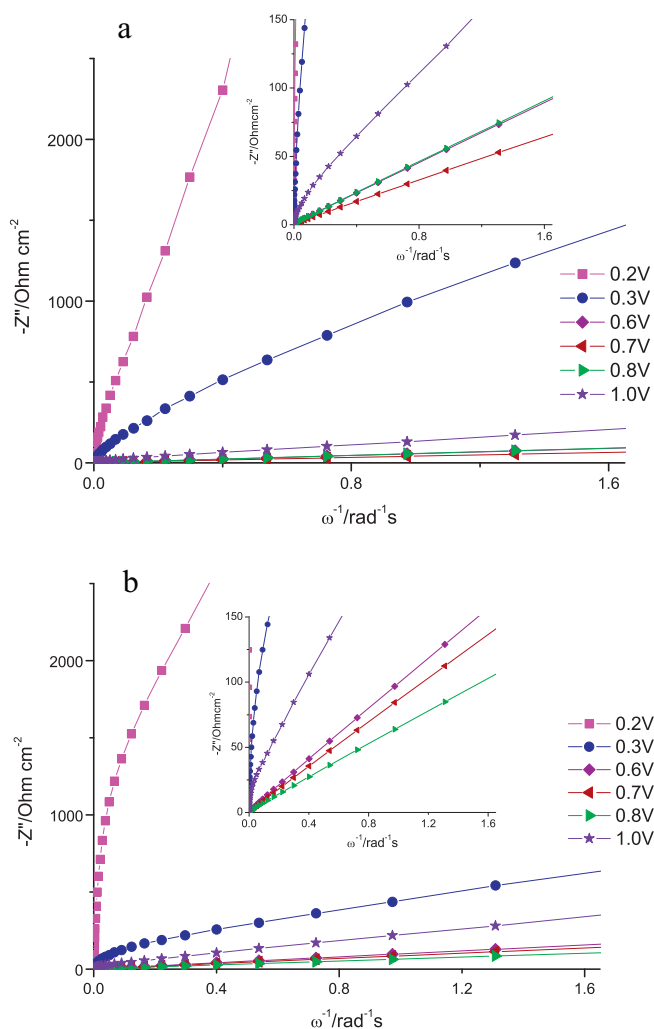
Fig. 7. Imaginary impedance constituent as a function of the reverse ac frequency for 1 μm thick polymer films. Potentials of spectra registrations are indicated on the graphs. (a) Poly-[Ni(CH$_3$O-SalPhen)] film. (b) Poly-[Ni(CH$_3$O-SaltmEn)] film.

Fig. 8. Low frequency capacities of polymer films. (a) Poly-[Ni(CH$_3$O-SalPhen)] film. (b) Poly-[Ni(CH$_3$O-SaltmEn)] film. Curves 1 and 2 correspond to calculations using Eqs. (4) and (6), conformably. On both figures, voltammograms of the 1 μm films recorded at 50 mV/s are presented for reference.

imaginary impedance constituent Z'' and angular frequency ω is observed in a wide interval of potentials excepting those which conform to the beginning of the second redox transition within the corresponding film. In our opinion, this is not a surprising fact, since a more complicated equation than Eq. (4) should, in general, be applied for such regions accounting for the above mentioned necessity of introducing three kinds of charge carriers for these intervals of electrode potentials. Besides, one can also account for a possible contribution of injection steps to the impedance constituents obtained at these conditions, which seems similar to the effect registered earlier at such potentials in scope of CV measurements with varying sweep rate v. However, to characterize changes of the low-frequency capacity corresponding to these intervals, we used the slopes of the $Z''(\omega^{-1})$-dependencies observed experimentally at frequencies $\omega \leq 6$–5 rad/s (see Fig. 7a and b, curve 1) not taking into account the fact of their non-zero extrapolation in the limit of $\omega \to \infty$. Some basis for such a treatment of the obtained abnormal $Z''(\omega^{-1})$-dependencies will be given later. Now, we only add that the same effect of non-linearity of $Z''(\omega^{-1})$-dependencies was observed also in case of non-substituted ligands, but it was weakly expressed and observed in a more narrow range of electrode potentials [13].

Capacities C_{LF} of both kinds of the films are represented as functions of electrode potential E in Fig. 8a and b (curve 1). It
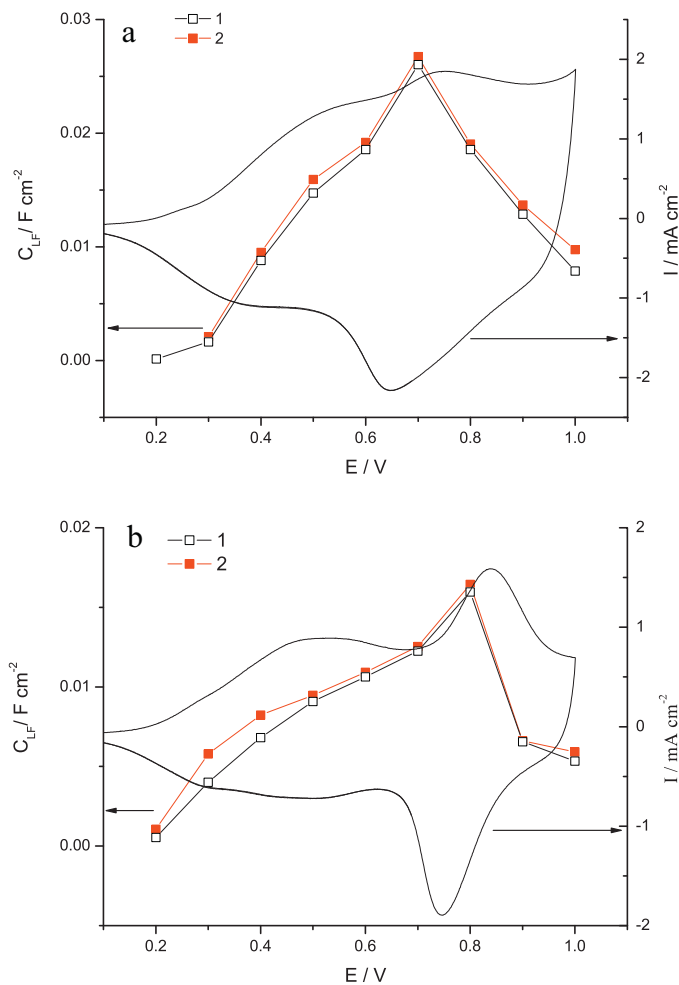
is seen that, as it should be according to Eq. (5), in both cases of different Ni complexes, capacities $C_{LF}(E)$ have an extrema. The latter is also in agreement with Eq. (5), since the peak potentials (about 0.7 and 0.8 V for poly[Ni(CH$_3$O-SalPhen)] and poly[Ni(CH$_3$O-SaltmEn)] complexes, conformably) are in the range, where the second redox transition predominantly proceeds, at least in the case of poly[Ni(CH$_3$O-SaltmEn)] films. For both polymers in question, an additional shoulder of the $C_{LF}(E)$-dependence is observed at $E \approx 0.6$ V, which indicates on the existence of one more redox transition proceeding at this and more positive electrode potentials. Such shape of $C_{LF}(E)$ dependences corresponds to the splitting of voltammetric peaks for both types of films in question. It should also be noted that for 2 μm films values of C_{LF} are two times higher than for 1 μm films, so the specific capacities are equal for the films of different thickness. Thus, the data obtained on the low-frequency capacities are in a qualitative accordance with the used theoretical representations and confirm the previous results of CV measurements. The latter is also reaffirmed by the established vicinity of the maximum specific capacities $C_{LF}(E_p)/L$ (260 F/cm^3 for poly[Ni(CH$_3$O-SalPhen)] and 160 F/cm^3 for poly[Ni(CH$_3$O-SaltmEn)]) to those obtained from CV-data (about 190 and 125 F/cm^3, correspondingly).

Turning to the impedance results obtained in case of more high ac frequencies (up to $f \approx 1$ kHz), we remind the above indicated fact that the expressed Warburg's behavior of the impedance
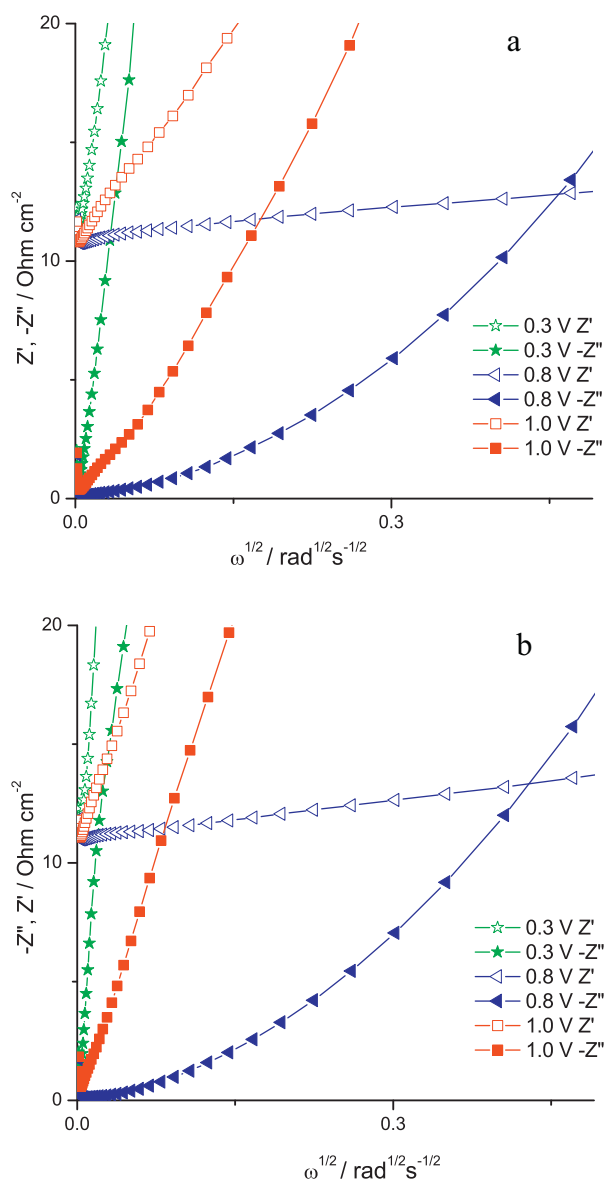
Fig. 9. Real and imaginary impedance constituents as functions of the reverse square rooted frequency for 1 μm thick polymer films. Potentials of spectra registrations are indicated on the graphs. (a) Poly-[Ni(CH3O-SalPhen)] film. (b) Poly-[Ni(CH3O-SaltmEn)] film.

Fig. 10. Warburg constants of 1 μm thick polymer films. (a) Poly-[Ni(CH3O-SalPhen)] film. (b) Poly-[Ni(CH3O-SaltmEn)] film. Curves 1 and 2 correspond to calculations using Eqs. (4) and (6), conformably. On both figures voltammogramms of the 1 μm films recorded at 50 mV/s are presented for reference.

constituents for both kinds of the films was observed only at potentials about 0.3–0.4 V and 1.0 V. For other potentials, we used an explicit representation of both constituents as functions of the reciprocal square root frequency, $\omega^{-1/2}$ (see Eq. (3)), which, as it took place for non-substituted ligands [13], allowed us to extract the Warburg parts of the recorded impedance constituents. Typical examples of such a handling of the obtained impedance results are given in Fig. 9a and b. As one can see, in some cases, the performed extraction of the Warburg constituents seems questionable, since linear parts of dependences $-Z''(\omega^{-1/2})$ and $Z'(\omega^{-1/2})$ occur to be so short, that only some tangents to the corresponding curves might be constructed. However we calculated the values of the Warburg constant, σ_W (i.e. slopes $d(-Z'')/d(\omega^{-1/2})$ and $dZ'/d(\omega^{-1/2})$) using the slopes of the both dependences indicated. The results of such calculations are given in Fig. 10a and b (curve 1). From these figures it can firstly be seen that in both cases such determinations give very similar values of the Warburg constant. In addition, these values appear to be practically independent on the film thickness,
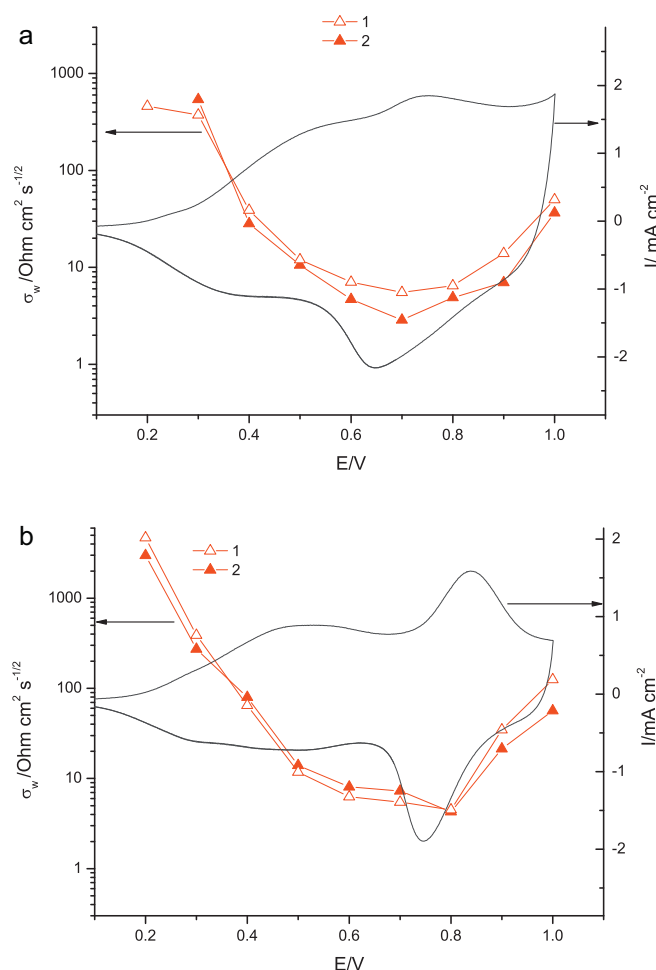
as they should be according to Eq. (3). Although these circumstances, it seems, point to a reliable character of the performed determinations, we will further apply an alternative handling of the discussed data in order to check regularity of the obtained values of σ_W.

Prior to a use of such handling, we once again emphasize that the above uncertainty in the Warburg constant determinations takes place in the ranges of overlapping redox transitions, i.e. the conditions, in which abnormal low-frequency dependencies of the imaginary impedance constituent, $Z''(\omega^{-1})$, are observed (see above). This determined our desire for a more detailed analysis of the established dependencies. In particular, we established that the above curvilinear low-frequency dependencies of the imaginary impedance constituent become linearly dependent on $\omega^{-1/2}$ in the indicated region of overlapping redox transitions if one uses the coordinates: $-\omega^{1/2}Z''$ versus $\omega^{-1/2}$ (see Fig. 11). This finding points to the existence of a mixed case of the frequency dependent impedance, in the conditions of which both the Warburg and the pseudo-capacity impedance constituents are simultaneously observed. So, using the same notations as those defined previously, the impedance in the discussed region of overlapping redox transitions can be represented as follows

$$Z(\omega) = Z'(\infty) + \frac{(1-j)\sigma_W}{\omega^{1/2}} - \frac{j}{\omega C_{LF}} \qquad (6)$$
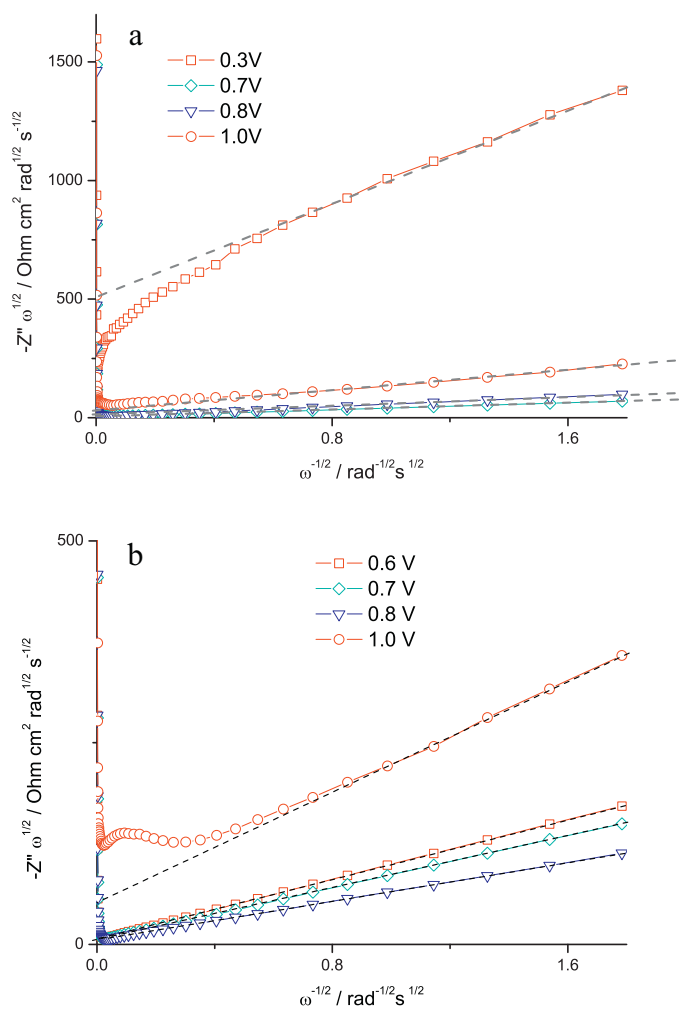
Fig. 11. Imaginary impedance constituent becomes linearly dependent on the reciprocal square rooted ac frequency using coordinates – $\omega^{1/2}Z''$ versus $\omega^{-1/2}$. (a) Poly-[Ni(CH$_3$O-SalPhen)] and (b) poly-[Ni(CH$_3$O-SaltmEn)] films of 1 μm thickness. Potentials of spectra registrations are indicated on the graphs.

Obviously, the established existence of the impedance dependencies given in Eq. (6) poses the question which reason is responsible for their appearance. From what has been said above, it seems that the necessary condition for their observation is the existence of two overlapping redox transitions. Their presence should be accompanied by some cross effects resulting from the presence of three kinds of charge carriers in the film interior. As will be shown in our subsequent paper, the impedance dependence satisfying Eq. (6) actually follows from the proper theoretical analysis. However at present, we cannot affirm that these results give the only explanation of the phenomenon in question, since a long list of possible explanations. In particular, we should indicate that the above discussed non-linearity of $Z''(\omega^{-1})$-dependencies in the range of low ac-frequency ω was observed not only in the case of non-substituted Schiff base ligands [13] mentioned previously, but also for modifying films formed from such substances, as hexacyanoferrate of indium [21], poly-o-phenylenediamine, and poly-o-aminophenol [22]. The appearance of such dependencies was previously explained by us in scope of the well-known representations on porous electrodes [23] and the capacity dispersion due to the presence of some traps (for example, ionic associates) within the film interior [24]. The same explanations might probably be used for the systems studied in this work.

Returning to Eq. (6), we indicate that such empirical dependence allows one to determine its parameters C_{LF}, σ_W and then

compare the obtained values with those found out in the way discussed above. It is important that the values of C_{LF} and σ_W calculated according to Eq. (6) are very close to those obtained previously by "classical" method (see curve 2 in Figs. 8 and 10, correspondingly). This, in our opinion, completely justifies the preceding ("classical") estimates of these parameters. It should also be added that the proposed data treatment seems much easier; only one linear fitting of low frequency data in coordinates – $\omega^{1/2}Z''$ vs $\omega^{-1/2}$ is sufficient to determine both the Warburg constant (intercepts of the lines) and capacity C_{LF} (reciprocal slopes of the same lines). The indicated self-consistence of the results obtained in two different ways allows one to calculate the effective diffusion coefficients of charge carriers within the studied films by using a constraint between the Warburg constant and the low-frequency capacity, namely the equation

$$\sigma_w = \frac{RT(t_e^2 + t_m^2)((1 + a_0\theta(1-\theta))/C\theta(1-\theta) + 1/z_x^2 c_x)}{F^2 A (2D_{ef})^{1/2}}$$

$$= \frac{(t_e^2 + t_m^2)L}{2C_{LF}(2D_{ef})^{1/2}}, \tag{7}$$

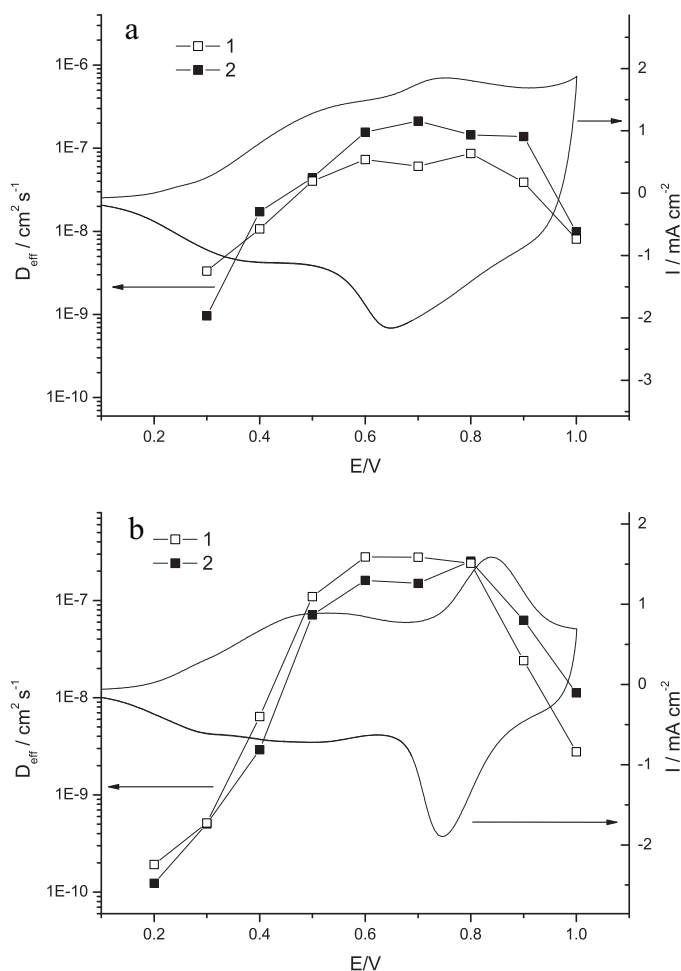**Fig. 12.** Effective diffusion coefficients as functions of the electrode potential. Average values for 1 μm and 2 μm thick films are represented. (a) Poly-[Ni(CH$_3$O-SalPhen)] films. (b) Poly-[Ni(CH$_3$O-SaltmEn)] films. Diffusion coefficients for curves 1 and 2 are calculated according to Eqs. (4) and (6), correspondingly. On both figures, voltammogramms of the 1 μm films recorded at 50 mV/s are presented for reference.

which produces

$$D_{eff} = \frac{1}{2}\left(\frac{(t_e^2 + t_m^2)L}{2\sigma_W C_{LF}}\right)^2 \tag{8}$$

Thus, one can estimate the effective diffusion coefficient by using values of the Warburg constant and the low-frequency capacity determined by the indicated methods. We performed such estimations and they led to practically coinciding results in the cases compared (see curves 1 and 2 in Fig. 12a and b).

Although the obtained values of D_{ef} seem to be reliable, we would like to emphasize their speculative character. The latter results from the above use of Eqs. (7) and (8), which are strictly valid only in case of films with two kinds of charge carriers. We can therefore conclude that charge transfer processes on electrodes modified by polymer films of Ni complexes with the Schiff bases are qualitatively described with the help of the existing theoretical representations, especially in the case of non-substituted ligands [13]. However, the established peculiarities related to the evident proceeding of several red/ox transitions within the studied films require a further development of the existing theory.

4. Conclusion

Summing up the obtained results, it seems possible to extract the following conclusions. Introduction of methoxy groups into aromatic parts of the Schiff bases affects the electrochemical properties of electrodes modified by polymer Ni complexes with these ligands. Such introduction slightly decreases the specific capacity of the compared films but essentially increases the solvent flows accompanying anion flows at the film charging (from 1–1.5 up to 3–4 solvent particles per one anion). In addition, it leads to noticeable splitting of CV-curves into two (at least) redox transitions, which are not revealed explicitly for non-substituted ligands. The origin of such splitting remains unclear, since all the polymers undergo one-electron switching according to the combined EQCM and coulometric data. Beside unusual voltammetric responses, abnormal frequency dependences of the impedance constituents are observed in the case of substituted ligands within the range of electrode potentials between overlapping redox transitions. In particular, the simultaneous presence of the Warburg and quasi-capacitive frequency dependences occurs inherent to the imaginary impedance constituent within the above indicated range of electrode potentials. In our opinion, such peculiarities of electrodes covered by polymer complexes with substituted ligands result from the presence of three kinds of charge carriers within the modifying films. This makes desirable some generalization of the voltammetry and impedance theory on the case of the systems in question.

Acknowledgments

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