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# Interaction of polyaniline and transition metal salts: formation of macromolecular complexes

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## Summary

Conditions for complex formation of some transition metal salts and emeraldine base of polyaniline were investigated, and the obtained macromolecular complexes have been characterized by the UV-Vis-IR spectroscopy. It was found that complex formation conditions are dependent on both the cation and anion of the inorganic salt used, as well as on the solvent environment. In some cases, formation of the complex occurred in the form of a precipitate directly in the solution. In other cases, no precipitate was observed in the solution, however, the complex was recognized during film casting from the polyaniline – inorganic salt solution. Electronic absorption spectra for both precipitates and films for the majority of samples possessed features characteristic of the protonated, emeraldine salt form of the polymer. However, IR absorption spectra were different from the protonated polyaniline form. Based on the obtained data, the model of the macromolecular polyaniline - transition metal salt complex is proposed.

## Introduction

The problem of interaction of conductive polymers, particularly polyaniline (PANI), and metal atoms or metal cations is of great importance due to the growing use of this polymer in organic electronics [1], electroluminescent devices [2,3], as protective coating against corrosion of metal surfaces [4,5,6], *etc.* One of the key problems in these fields is to understand the mechanism of the formation of PANI / metal heterojunctions. For purposes of organic electronics, for example, it is important to know whether the polymer film can create an ohmic junction with the contacting metal electrode. It was reported that some metals, for example tin and copper, form excellent ohmic contacts to films of the emeraldine salt (ES) form of PANI [7]. Aluminum / ES junctions, by contrast, were found to have slight rectifying properties [8]. It should be noted that in the case of organic polymer/ metal heterojunctions, knowledge of the work function of the contacting materials is not sufficient for prediction of whether the contact will be ohmic or rectifying, because in many cases chemical reactions at the interface take place [9-11], which drastically modify the electronic properties of the organic semiconductor. However, no systematic studies of PANI / metal heterojunctions and PANI - metal atoms or metal cations interactions have been performed so far.

On the other hand, interactions of PANI with metal ions give rise to novel catalytic, luminescent and other properties of the complex formed. It was reported that PANI can interact with many heavy metal ions such as $Pd^{2+}$ [12], $Zn^{2+}$ [13], $Fe^{3+}$, $Sn^{4+}$[14], $Au^{3+}$ [15], rare-earth cations [16,17]. However, there are no full details on mechanisms of PANI – metal cation interactions. The goal of this work is to contribute to the understanding of formation of PANI - metal salt complexes and PANI – metal cations interactions.

## Experimental

Emeraldine base (EB) of polyaniline was dissolved in dimethylformamide (DMFA) to prepare saturated (~ $10^{-3}$ M) dark-blue solution of the polymer, followed by sonication and filtering of the solution to remove undissolved particles. Salts of transition metals were dissolved in DMFA to prepare solutions with desirable concentration. The following salts have been used in this study: $Cr_2(SO_4)_3$, $FeSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, $Ni(NO_3)_2$, $La(NO_3)_3$, $MnCl_2$, $FeCl_3$, CuCl, $CuCl_2$, $LaCl_3$, $EuCl_3$.

In a similar way, the EB powder was dissolved in N-methylpyrrolidinone (NMP) to prepare solution with concentration of ~ $10^{-2}$ M. Salts of $FeSO_4$, $NiCl_2$, $CuCl_2$, $EuCl_3$, $LaCl_3$, $La(NO_3)_3$ were dissolved in NMP to prepare solutions with desirable concentrations.

EB-metal salt complexes have been prepared by mixing the EB and salt solutions with certain proportion of EB (calculated per tetramer units) to metal ions. The mixtures were left in the closed vessels for a period of a few minutes to a few days until a dark precipitate has been formed. This precipitate was then collected, dried and studied by the UV-Vis-IR spectroscopy. If no precipitate has been observed in the mixture, the solutions were used for preparation of films by casting onto a quartz plate.

In order to take electronic absorption spectra from the precipitate, it was collected onto a glass plate and subjected to measurements in the diffusion reflection mode, using a collecting sphere. Pellets of the MgO powder served as a reference. Films prepared by casting were measured in the transmission mode, bare quartz plate served as a reference.

In order to take IR absorption spectra from the precipitate, it was mixed with the KBr powder and pressed as pellets. Films for IR measurements were cast onto germanium plates. The measurements of the samples were performed in the transmission mode.

Spectrophotometers SPECORD M40 and SPECORD M80 were used for the measurements in the UV-Vis and IR ranges, respectively. Measurements have been performed in the ranges of characteristic absorption of the polymer, i.e. in the 330 nm to 800 nm region and in the 1700 $cm^{-1}$ to 700 $cm^{-1}$ region, respectively.

## Results and discussion

Upon mixing the EB and salt solutions, formation of a precipitate in a few minutes has been observed for some combinations of the polymer and inorganic salts. This indicates that interaction of the polymer and inorganic ions takes place in the solution, which results in the formation of an insoluble polyelectrolyte in the solution. Appearance of the precipitate was dependent on both metal cation and counter-ion of the salt used, as well as on the solvent employed. Most transition metal chlorides gave rise to formation of insoluble precipitates in a few minutes after addition to the DMFA solution of the polymer. However, no precipitate was observed with the $EuCl_3$ salt in the DMFA solution. Use of different salts with the same metal cation was found can give different results. For example, addition of the $LaNO_3$ salt to the DMFA solution of EB did not result in formation of any precipitate, whereas use of the $LaCl_3$ salt yielded a dark-green precipitate in a few minutes. At the same time, it was observed that formation of precipitates with the same cation, for example that of copper or iron, and different anions (chloride and sulphate) takes place in DMFA solutions, that indicates that the metal ion plays an important role in the formation of a complex with the polymer.

It has been observed that on using the same counter-ion, the efficiency of the formation of a precipitate was strongly dependent on the metal cation used. For $SO_4^{2-}$ anion, the best precipitation was obtained with $Cu^{2+}$ and $Fe^{2+}$ cations, while use of $Zn^{2+}$ cations did not result in formation of any observable precipitate in DMFA solutions.

Kinetics of the formation of the precipitates was also dependent on the metal ion-to-EB relationship. Rapid formation of the precipitate was observed with excess of the metal ion - EB (tetramer) stoichiometric ratio. Normally, good results were obtained at approximately 100:1 ratio of metal ions to the EB (tetramer) in DMFA solutions. Upon decreasing the above relationship delaying kinetics of the precipitate formation was found. In order to determine how many cations were involved in the formation of the precipitate per each unit of the EB, it was prepared five $FeSO_4$/EB mixtures in DMFA, with different molar ratios of $Fe^{2+}$ to EB (tetramer), namely 100:1, 10:1, 4:1, 2:1 and 1:1. In a few weeks, when the reaction between EB and salt has been completed and all the complex has been precipitated, the color of the solutions changed and became red, reddish-brown, colorless (very light green), colorless (very light blue) and light-blue, respectively. The color of the first mixture is typical of the $FeSO_4$ solution, i.e. it indicates the excess of the $FeSO_4$ in the mixture, while the blue color is indicative of the polymer excess in the solution. Since only colorless solutions are indicative of a stoichiometric $Fe^{2+}$/ EB ratio, one can conclude that one metal ion attacks one or two benzenoid and quinoid groups in the polymer backbone (Fig.1).

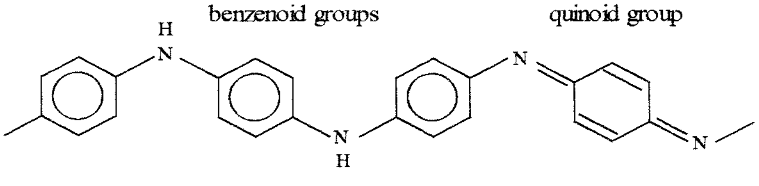

Fig.1. Molecular structure of a tetramer unit of the emeraldine base of polyaniline.

Change of the solvent resulted in drastic changes of the conditions for formation of precipitates. Use of NMP as a solvent resulted in formation of the precipitate only for the EB – copper salt mixtures. Other inorganic salts were found do not yield precipitate upon addition to the NMP solution of the polymer. However, upon casting of the EB-inorganic salt film from the NMP solution, color of the formed film was found to differ from that of the pure EB film, even if the colorless salt solution, for example that of $LaCl_3$, was used. These results point out that the NMP is a good solvent to dissolve macromolecular complexes formed, while DMFA is not.

Electronic absorption spectra taken from precipitates prepared with different transition metal salts, except for copper salts, showed spectral features characteristic of the ES, i.e. the features of the polymer in the protonated form (Fig.2). However, the polymer

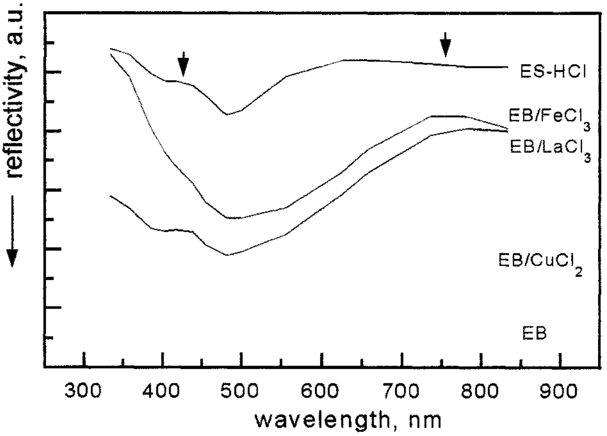

Fig. 2. Diffusion reflection spectra of the EB powder, EB-HCl and EB-transition metal salt precipitates from DMFA solutions. Arrows indicate appearance of the polaron absorption features.

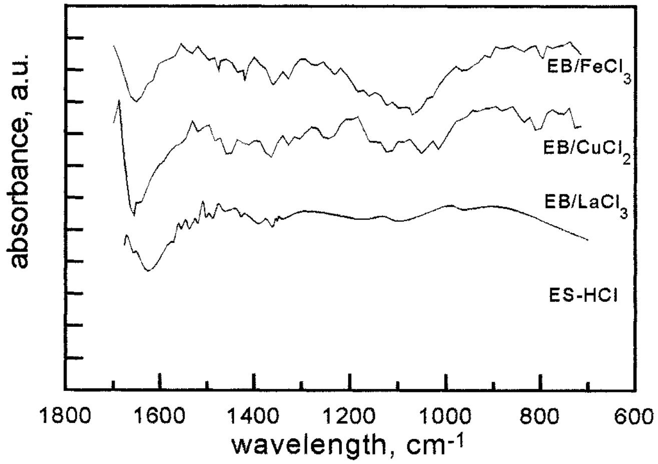

Fig.3. IR absorption spectra of the EB-HCl and EB-transition metal salt precipitates.

complex based on Cu salts showed UV-Vis absorption spectra characteristic of the oxidized form of PANI, pernigraniline base.

IR absorption spectra of the precipitates obtained from DMFA solutions, showed some similar features which are independent on the transition metal used (Fig.3). The spectra have a strong wide absorption band in the range of 1580 to 1700 cm$^{-1}$, followed by smaller peaks centered at ~1460 cm$^{-1}$, ~1420 cm$^{-1}$, ~1360 cm$^{-1}$, ~1240 cm$^{-1}$, ~800 cm$^{-1}$ and a wide smeared absorption profile around 1100 cm$^{-1}$. Spectra of the EB/La complex, however, showed absence of the 800 cm$^{-1}$ peak. The IR spectrum of the EB-$CuCl_2$ precipitate obtained from NMP solution was quite similar to its counterpart obtained from the DMFA solution, except for the last band which is strongly broadened and centered at 844 $cm^{-1}$ in the precipitate obtained from NMP solution. The band at ~1660 $cm^{-1}$ was found to become greatly diminished after annealing of the sample at $60^0C$ for a few hours, when part of solvent molecules becomes removed from the sample. This result points out that the common feature in the IR spectra of the precipitates, the band in the region of 1580 to 1700 $cm^{-1}$, can be attributed to solvent molecules which are bound to the complex formed.

We cannot give here further detailed analysis of the IR bands of the precipitates. However, we should note the great difference of the above spectra and spectra of the polymer without transition metal salts. The IR spectrum of the ES precipitate prepared in a similar way in DMFA solution, was found to greatly differ from spectra of the other precipitates. Major peaks of the ES precipitate (Fig.3) were observed at 1588 $cm^{-1}$, 1468 $cm^{-1}$, 1404 $cm^{-1}$, 1256 $cm^{-1}$, 1024 $cm^{-1}$, 884 $cm^{-1}$ and 868 $cm^{-1}$. IR absorption features of the EB powder (not shown) were found to differ from those of the EB-transition metal salt precipitates also. Such a difference in spectra of the EB and ES on one hand, and precipitates of EB-transition metal salts on the other hand, points out the change in molecular symmetry of the polymer - transition metal salt complex as compared with the EB or ES form of the polymer. It seems that the metal ion - polymer interaction causes charge density redistribution over the polymer chain or chain conformations.

It should be noted that the IR spectra of films cast from the NMP solutions, where no precipitate was observed, were very similar to those of pure EB films cast from the NMP solution (not shown). This result indicates that the complexation of the polymer and inorganic salts occurs in two different ways. Formation of an insoluble precipitate as a result of the complexation implies specific arrangement (packing) of the polymer chains and inorganic ions inside the precipitate formed. In the other case, salt molecules interact with the polymer molecules as a result of solvent removal from the sample, so that such an interaction does not affect arrangement of the polymer chains strongly.

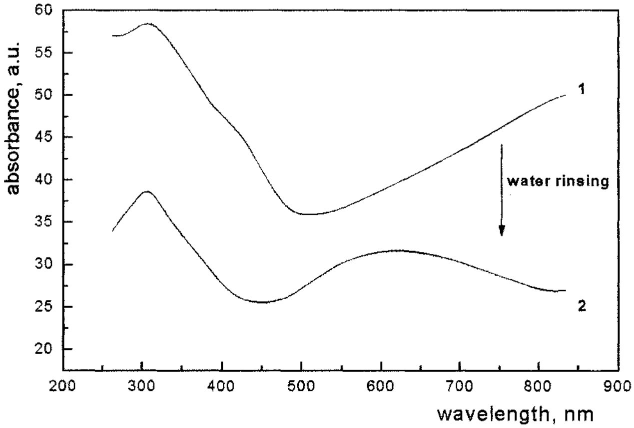

Fig.4. Electronic absorption spectra of the EB/ $EuCl_3$ composite in the form of (1) as-prepared film cast from DMFA solution, and (2) after rinsing this film with distilled water.

In that cases when the solutions did not yield precipitates, changes in electronic absorption spectra of the mixtures nevertheless were found upon formation of a film by casting. For example, blue color of the EB/$EuCl_3$ solution changed for light-green when a film cast from the solution was formed. Such a change points out complexation of the transition metal salt and polyaniline in the solid state. Electronic absorption spectrum of the film (Fig.4) was similar to that of the ES, i.e. indicates formation of the polaron lattice in the polymer backbone upon interaction of the EB and Eu salt. It should be noted that the formation of a transition metal salt - EB complex is reversible and that the pure EB form can be restored by treatment of the sample with distilled water. As shown in Fig.4, the spectrum of the $EuCl_3$/EB composite changed to that of the EB after rinsing the film with distilled water. This result points out that coupling between $Eu^{3+}$ cations and the polymer units is weak enough. A similar result has been found for other salt - EB samples.

Based on the data obtained we tentatively propose the molecular structure resulted from the polymer - transition metal salt interactions (Fig.5). This structure is based on the above findings that, first, one metal ion interacts with one or two ring units on the polymer backbone and, second, a polaron lattice in the polymer backbone should appear as a result of these interactions. This polaron lattice is very similar to that resulted from the protonic acid – EB interactions. However, intermediate conversions leading to the final structure should be different.

In principle, one can distinguish two tendencies for interactions of PANI in the emeraldine base form and metal cations. These two tendencies are due to existence of two groups in the polymer backbone, the benzenoid and quinoid groups, respectively (Fig.1). The first one is an electron-rich group which can donate an electron to the electron-accepting agent. This electron donor property of the benzenoid groups has been established earlier, for example it was shown that the charge transfer from the benzenoid unit of EB to a strong electron acceptor TCNQ occurs [18]. The oxidation of benzenoid groups of the polymer and reduction of metal ions, respectively, was also shown for interactions of EB with metal cations such as $Pd^{2+}$ [12], $Au^{3+}$ [15], $Eu^{3+}$ [17] in the solution. On the other hand, the quinoid group is an electron-deficient group which can be reduced by electron-rich agents. According to this classification, two types of interactions of the polymer with metal ions can be distinguished. The first one is the oxidation of the benzenoid group of EB by metal ions possessing relatively high electrode potential. This is the case for interaction of EB and $Cu^{2+}$, where metal cations become reduced and the polymer oxidized to pernigraniline base (PB), respectively, which is similar to interaction of EB with $Au^{3+}$ ions [15]. On the other hand, metal ions with low electrode potential have a tendency to reduce quinoid groups of the polymer. Alkali metal ions represent an extreme case of this tendency, resulting in pseudoprotonation of the imine nitrogen atoms of the EB [19,20]. Transition metal ions with intermediate values of the electrode potential appear to represent a class of materials whose ability to interact with PANI is twofold. They are able to oxidize the benzenoid group of EB and, on the other hand, they can coordinate to imine nitrogen atoms of the quinoid groups, similarly to pseudoprotonation of EB by $Li^+$ ions. Thus, the final structure can be a result of interactions of the transition metal cations with both benzenoid and quinoid units of the polymer chain, as shown schematically in Fig.5.

In this scheme, transition metal ions coordinate first of all to the amine nitrogen atoms (stage ii), followed by reduction of the metal ions and oxidation of the benzenoid groups of the polymer backbone (stage iii). However, after this stage of interaction,

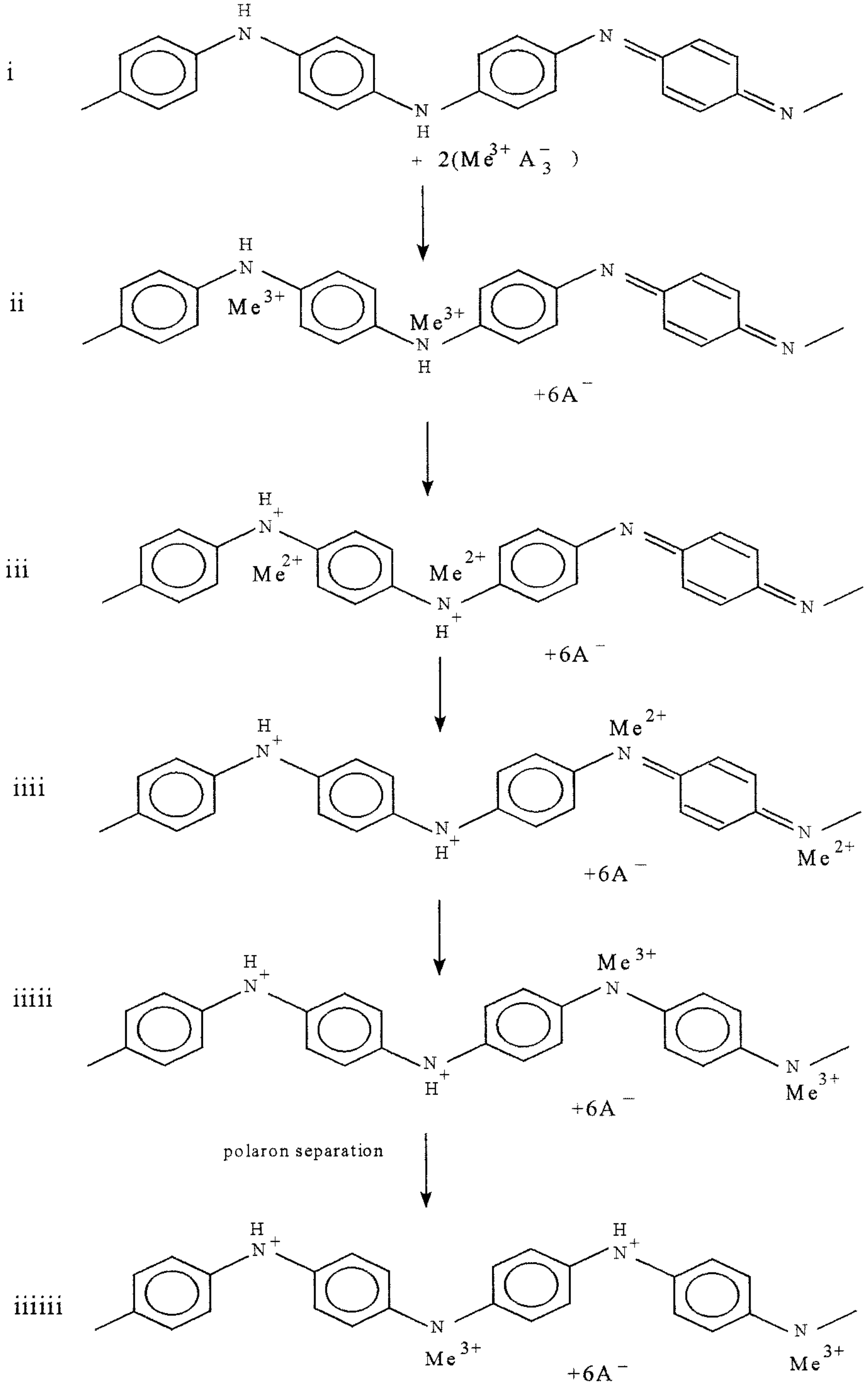

Fig. 5. Proposed scheme of the formation of the EB-transition metal salt complex. $Me^{3+}$ is the metal ion used, $A^-$ the counter-ion.

the metal ions move to electron deficient quinoid groups and coordinate to the imine nitrogen atoms (stage iiii) followed by reverse oxidation of the cations and reduction of the imine group of the polymer (stage iiiii), respectively. Finally, bipolarons formed on the polymer backbone separate due to electrostatic repulsion forces (stage iiiiii). In the proposed scheme, conversion of the EB chain to the polaron lattice occurs via two redox reactions, where metal ions serve as mediators for charge transfer from benzenoid to quinoid groups of the polymer.

## Conclusions

We have shown that the EB polymer is able to form a complex with a variety of transition metal salts. Solubility of the complex in DMFA is dependent on both the cation and anion of the salt used. The EB-to-metal ion interactions cause formation of a polaron lattice in the polymer backbone and change of the molecular symmetry of the polymer. The final molecular structure of the complex can be a result of the oxidation/ reduction redox reactions of the transition metal cations and the benzenoid/ quinoid units of the polymer backbone, respectively. Among transition metal cations used in this study, the copper ions have the highest electrode potential and result in oxidation of the polymer backbone only.

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