Polyaniline films doped with zinc salts and their properties

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It has been found that thin polyaniline films doped with several zinc salts in solutions at pH 5.5 become electroconductive and electroactive in neutral aqueous electrolytes. The shape of the voltammetric characteristics depends on the initial state of the film. The effect of "secondary doping" with *m*-cresol is observed for polyaniline complexes with zinc salt of camphorsulfonic acid.

Key words: polyaniline, secondary doping, zinc salts, camphorsulfonic acid, electrochemistry; absorption spectra, ESR; hysteresis, electroconductivity.

Polyaniline is one of the most promising conducting polymers. However, its application in contact with materials possessing low corrosion stability in acidic media, such as aluminum or zinc, is difficult, because acids are usually used as dopants.

It has been recently shown[1] that the introduction of polyaniline films into solutions of $ZnCl_2$ results in an increase in the electroconductivity and electroactivity in aqueous electrolytes at pH 5—6. It was of interest to elucidate whether similar phenomena are observed in solutions of other zinc salts.

Experimental

Polyaniline was obtained by the reaction of aqueous solutions (1 *M*) of ammonium persulfate and aniline perchlorate at pH 1. To decrease pH of the medium, 0.1 *M* $HClO_4$ was used. The polymer formed was washed with water, kept in a solution (0.1 *M*) of NH_4OH, dried, and dissolved in formic acid.

Thin polymer films were deposited by spin coating onto a glass substrate or carbon glass plates, which were used for the measurement of the electroconductivity and electrochemical studies. Contacts of silver paste were used to decrease the resistance.

Electroconductivity was determined by a Shch-402-M1 digital bridge. Voltammetric characteristics were measured in a standard three-electrode electrochemical cell using a PI-50-1 potentiostat. Zinc salts (analytically pure grade) were used without additional purification.

Results and Discussion

The data on the electroconductivity of thin films of polyaniline treated in solutions (1 *M*) of zinc halides and sulfate as well as in a saturated aqueous solution of camphorsulfonic acid are presented in Table 1. The surface resistance of the films was found to be somewhat higher than that reported previously,[1] which is related to their lesser thickness (≈0.5 μ) determined interferometrically. The values of the resistances are by approximately three orders of magnitude lower than those of the films preliminarily treated in solutions of KCl with pH 5.5. According to the preliminary data obtained by atomic absorption analysis, the polymer contains 0.72 zinc atoms per monomer unit consisting of two benzene rings and two nitrogen atoms.

It can be assumed that zinc salts, like solutions of acids, react with polyaniline to form the zinc—nitrogen bond. Therefore, it was of interest to study the changes in the optical and magnetic properties upon doping to compare them with the data obtained for the polymer doped with the acid. The absorption spectra of polyaniline in the visible range before and after the treatment with a solution (1 *M*) of zinc salt of camphorsulfonic

Table 1. Specific surface resistance of thin films of polyaniline doped with zinc salts

Coating	pH of solution	Resistance /Ohm cm^{-2}
Initial film	11.0	$2.45 \cdot 10^8$
KCl (1 *M*)	5.5	$2.80 \cdot 10^7$
$ZnCl_2$ (1 *M*)	5.5	$7.30 \cdot 10^4$
ZnI_2 (1 *M*)	5.7	$1.30 \cdot 10^5$
ZnF_2 (1 *M*)	5.6	$2.50 \cdot 10^5$
$ZnSO_4$ (1 *M*)	5.6	$1.37 \cdot 10^5$
HCl (1 *M*)	1.0	$6.30 \cdot 10^4$
Zn salt of camphorsulfonic acid	5.4	$3.10 \cdot 10^5$
Camphorsulfonic acid in acetonitrile	—	$2.25 \cdot 10^5$

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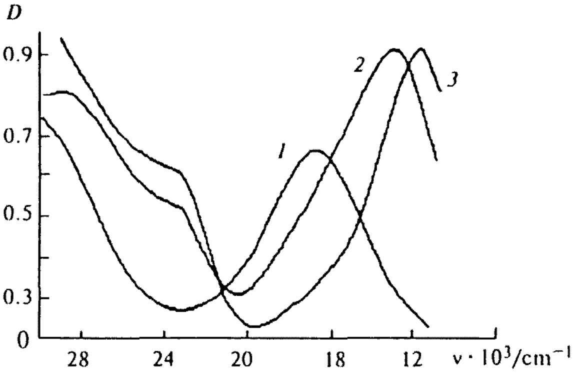

Fig. 1. Absorption spectra in the visible region: *1*, thin polyaniline film in the base form; *2*, thin polyaniline film doped with zinc salt of camphorsulfonic acid; *3*, the same film doped with *m*-cresol vapor.

acid are presented in Fig. 1. After this treatment, the films change their color from blue, which is characteristic of the nonconducting form, to green typical of conducting polyaniline. A similar effect is observed for all other salts.

Let us consider in detail the "secondary doping" effect, which lies in the fact that there are additives of another type along with usual dopants (which act as oxidizing or reducing agents and result in the formation of radical cation salts). They do not possess redox properties, but they affect substantially the properties of the polymer formed. For example, when polyaniline salts with camphorsulfonic acid are treated in *m*-cresol, the long-wave absorption band shifts to the infrared region, and the electroconductivity of the films increases. This effect is explained by a decrease in the electrostatic interaction of the primary dopant with the polyaniline macromolecule, which results in untwisting of the polymer ball under the action of the electrostatic charge.[2] This, in turn, decreases the concentration of defects in the polymer chain. It is established that a similar phenomenon is observed when the complex based on polyaniline and zinc salt of camphorsulfonic acid is treated with vapor of *m*-cresol. As follows from Fig. 1, the maximum of the long-wave peak shifts drastically to the low-frequency range. The discoloration of the film, which gains pale lettuce-green color, is distinctly seen. The pressure of water vapor exerts no effect on the electroconductivity of the sample obtained, while a change in the moisture content changes, sometimes by a factor of five to ten, the electroconductivity of polyaniline, because water is a natural "secondary dopant."

The treatment of polyaniline with solutions of zinc salts results in the appearance of the intense ESR signal with a distance between peaks of 3.2 G. This signal (Fig. 2) is similar to that appeared upon doping of polyaniline with acids, although its width is somewhat greater. The change in the form and an increase in its intensity by more than an order of magnitude testify that the charge transfer occurs when the polymer film is introduced into a solution of the salt.

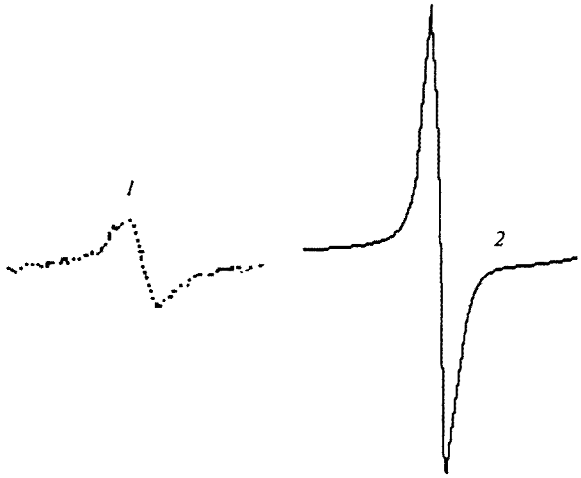

Fig. 2. ESR spectra: *1*, polyaniline film in the base form; *2*, polyaniline film doped in a solution (1 *M*) of $ZnCl_2$ at pH 5.5.

Polyaniline layers applied to carbon glass possesses pronounced electroactivity in solutions of zinc salts. The voltammetric characteristics of polyaniline in a solution of zinc sulfate at pH 5.5 are shown in Fig. 3. The shape of the voltammetric curve depends substantially on the form of polyaniline. If the base is used as the starting form, the voltammetric curve is blurred; in the case of the acid form equilibrated with a solution of pH 5.5 for several days, sufficiently narrow peaks are observed. The same shapes of voltammetric curves are obtained when a solution of zinc fluoride is used. The difference in the shape of voltammetric characteristics is also observed in the case of solutions of $ZnCl_2$, but it is not as substantial as in the previous cases.

It should be noted that polyaniline samples doped with zinc salts and acids are similar. The changes in the electroconductivity and optical and magnetic properties

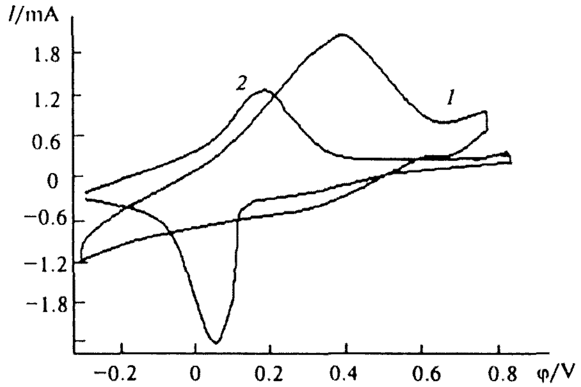

Fig. 3. Voltammetric characteristics of the polyaniline film in a solution (1 *M*) of $ZnSO_4$ at pH 5.5: *1*, initial film in the base form; *2*, initial film in the acid form.

indicate unambiguously the formation of the radical cation complex, and polyaniline and zinc salts act as a donor and acceptor, respectively. The values of the surface resistance are presented in Table 1. The specific values for the polyaniline films doped with zinc salts are 2 to 15 Ohm cm^{-2}.

It should be mentioned in the discussion on the nature of the electrochemical reactions occurring upon the oxidation—reduction of polyaniline that it is difficult to determine the nature of an ion that compensates the charge of the film. According to the preliminary data, the redox transition at pH 3 is accompanied by the transfer of zinc ions to or from a solution of the electrolyte. Now it is difficult to rule out the possibility of the participation of salt anions or protons present in the solution in this process. An attempt to study the dependence of the redox potential on the salt concentration is associated with the difficulties caused by the necessity to introduce neutral salts in order to maintain the electroconductivity and the ionic strength of the electrolyte. These salts possess electroactivity and blur or shift the peak of the voltammetric curve.

The effect of the initial state of the polyaniline film on the shape of the voltammetric curve can be explained by the difference in the structures of the base and acid forms of polyaniline. It now has been reliably proved that the transition of the film to the acid form is characterized by the formation of ordered "metallic islands" or domains. Thus, when the basic form is used, the structure of the material is amorphous, while for the acid form the structure is crystalline. The effect of zinc doping on the structure of the amorphous material is not clear so far. Perhaps, in this case, there is a new effect of memory inherent in polyaniline films.

The possibility of the realization of the "secondary doping" effect is of basic significance, because it allows one to assume that polyaniline doped with zinc films can be transformed into the highly conducting metallic state.

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