

Lewis Acid Doped Polyaniline. Part II: Spectroscopic Studies of Emeraldine Base and Emeraldine Hydrochloride Complexation with FeCl₃

Françoise Genoud,^{†,‡} Irena Kulszewicz-Bajer,[§] Alexandre Bedel,[†]
Jean Louis Oddou,^{‡,||} Claudine Jeandey,^{||} and Adam Pron^{*,†}

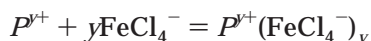
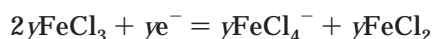
Laboratoire des Métaux Synthétiques, UMR 5819, DRFMC-CEA Grenoble, 38054 Grenoble Cedex 9, France; Université Joseph Fourier, Grenoble, France; Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00664 Warszawa, Poland; and Laboratoire de Chimie de Coordination, URA 1194, DRFMC-CEA Grenoble, 38054 Grenoble Cedex 9, France

Received July 29, 1999. Revised Manuscript Received December 2, 1999

It is demonstrated that Lewis acid doping of polyaniline in the oxidation state of emeraldine can be conveniently monitored by ⁵⁷Fe Mössbauer spectroscopy if FeCl₃ is used as the dopant. The spectrum of doped polyaniline consists of two doublets with distinctly different Mössbauer parameters which can be unequivocally ascribed to two types of complexing sites (amine and imine nitrogens). From the temperature dependence of the isomer shift and the recoil free absorption, we have calculated Mössbauer lattice temperature Θ_m' as probed by both complexing sites, which were 83 K for the amine and 126 K for the imine sites. These low values of Θ_m' imply significant mobility of the dopant at temperatures close to room temperature, which is typical of small molecules inserted into polymer matrices. FeCl₃-doped polyaniline is soluble in nitromethane, and acetonitrile and films cast from these solvents show conductivity of 0.2 S/cm. FeCl₃-doped polyaniline is also a strong near-infrared absorber.

Introduction

Ferric chloride became a popular doping agent for the majority of conducting polymers after the discovery that polyacetylene can be rendered conductive by its treatment with FeCl₃–nitromethane solutions.¹ In conducting polymers which undergo an oxidative type of doping, the reaction with FeCl₃ is a redox reaction assisted by an acid–base process:^{2,3}



In the above reaction scheme, half of the FeCl₃ molecules involved act as an oxidizing agent transforming neutral polymer chains into polycarbonium cations, whereas the second half behave like a Lewis acid being complexed by Cl⁻ to give the FeCl₄⁻ complex anion. During the doping reaction, FeCl₄⁻ anions are inserted

into the polymer matrix in order to compensate for the positive charge imposed on the polymer chain as a result of the redox process. This type of redox process has been reported for polyacetylene, poly(*p*-phenylene)polypyrrole, polythiophene, and their derivatives. It can also account for the oxidative doping of leucoemeraldine, the most reduced form of polyaniline.

One is tempted to verify whether FeCl₃ can be used as the dopant for emeraldine, i.e., the partially oxidized form of polyaniline. In this case, one cannot expect a redox type of doping as described above because ferric chloride is not a sufficiently strong oxidizing agent to oxidize emeraldine. It is however possible to take advantage of the facts that emeraldine is a Lewis base with two complexing sites (amine and imine nitrogens) and FeCl₃ exhibits Lewis acidity. Thus, Lewis acid complexation (Lewis acid doping) of polyaniline may be expected for emeraldine–FeCl₃ system.

Literature data on polyaniline doping with Lewis acid are scarce.⁴ The overwhelming majority of the research is devoted to Brønsted acid doping (protonation) of this polymer.⁵ It should be however noted that the chemical and spectroscopic properties of Lewis acid doped emeraldine are significantly different from those of protonated emeraldine. In our previous paper,⁴ we demonstrated that emeraldine doped with SnCl₄ can be

[†] UMR 5819.

[‡] Université Joseph Fourier.

[§] Warsaw University of Technology.

^{||} Laboratoire de Chimie de Coordination.

[†] Laboratoire des Métaux Synthétiques.

(1) Pron, A.; Kulszewicz, I.; Billaud, D.; Przyluski, J. *J. Chem. Soc., Chem. Commun.* **1981**, 783.

(2) Pron, A.; Zagorska, M.; Kucharski, Z.; Lukasiak, M.; Suwalski, J. *Mater. Res. Bull.* **1982**, *14*, 1505.

(3) Kitao, S.; Seto, M.; Maeda, Y.; Matsuyama, S.; Masubuchi, S.; Kazama, S. *J. Phys. Soc. Jpn.* **1997**, *66*, 1195.

(4) Kulszewicz-Bajer, I.; Pron, A.; Abramowicz, J.; Jeandey, C.; Oddou, J.-L.; Sobczak, J. *Chem. Mater.* **1999**, *11*, 552.

(5) For example, see: Trivedi, D. C. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, p 505.

dissolved in nitromethane or acetonitrile, i.e., solvents which dissolve neither emeraldine base nor its protonated form. To characterize the complex formed, we used ^{119}Sn Mössbauer spectroscopy. We were however unable to differentiate between two nonequivalent complexing sites (imine and amine) because in the case of ^{119}Sn Mössbauer spectroscopy the line widths do not allow for a good resolution of the spectra.

From this point of view, the complexation (Lewis acid doping) of emeraldine with FeCl_3 is advantageous. ^{57}Fe Mössbauer spectroscopy in general gives well-resolved lines, which in appropriate conditions can be attributed to chemically nonequivalent environment of iron nuclei under investigation.

The main purpose of this research was to prepare a new form of doped polyaniline (emeraldine- FeCl_3 complex) and to study dopant-polymer interactions using complementary spectroscopic techniques such as Mössbauer, EPR, and UV-vis-NIR spectroscopies.

Experimental Section

Synthesis of Polyaniline. Polyaniline was synthesized at -15°C in an $\text{HCl}/\text{LiCl}/\text{water}/\text{ethanol}$ solution using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidizing agent. The obtained polyaniline hydrochloride was then converted to the base form by treatment with an excess of 0.3 M NH_3 (aq) solution. The inherent viscosity of the obtained polymer was measured at 25°C in 0.1 wt % solution in sulfuric acid using an automatic Ubbelohde viscosimeter. The obtained value was 1.7 dL/g. The detailed polymerization procedure can be found elsewhere.⁴

Doping of Polyaniline with FeCl_3 . Doping of emeraldine base with FeCl_3 was carried out using classical high-vacuum-line techniques. In a typical procedure, 269 mg (1.65 mM) of anhydrous ferric chloride was dissolved in 20 mL of freshly dried nitromethane and mixed with 150 mg (1.65 mM) of carefully vacuum-dried emeraldine base. The doping was carried out for ca. 15 h. Lewis acid-base complexation rendered polyaniline soluble in nitromethane which manifested itself by a deep blue coloration of the doping medium and the gradual disappearance of the polyaniline base powder.

Solutions of Lewis acid doped polyaniline have film-forming properties. Free-standing films were obtained by evaporation of the solvent. Such films were washed with pure nitromethane and pumped in a vacuum line until a constant mass was reached.

One of the goals of the present research was to differentiate spectroscopically between two types of complexing sites. To resolve this problem, we have prepared samples in which imine nitrogen complexing sites were blocked by protonation with HCl and the Lewis acid-base complexation could occur only on amine sites. Such samples can be prepared by protonation of emeraldine base in 1 M HCl solutions. It is known⁶⁻⁸ that in this case imine nitrogens are protonated preferentially. Moreover, amine site protonation is unstable with respect to extending pumping. For this reason, the protonation level of polyaniline pumped to constant mass is equal to the fraction of imine nitrogen in the polymer and may vary from 0.40 to 0.60 depending on the changes in the polymerization procedure. The protonation level can be extracted from the analytically determined Cl/N molar ratio. In our case, the elemental analysis gave the following formula: $\text{PANI}(\text{HCl})_{0.43}(\text{H}_2\text{O})_{0.65}$. HCl-protonated polyaniline contains significant amount of

water which solvates counterions entering the polymer matrix.⁹ It is therefore necessary to carefully dehydrate the samples before FeCl_3 doping. For the dehydration, we have used SOCl_2 , which is a convenient drying agent since it is volatile and the products of its hydrolysis are also volatile. It should be noted here that one of the product of polyaniline drying with SOCl_2 is HCl, which in turn can locally increase its protonation level. However, since the sample is protonated to saturation with respect to imine sites and amine-site protonation is not stable with respect to dynamic pumping, the treatment with SOCl_2 should not change the protonation level provided that the samples are pumped to constant mass. We have verified this experimentally. Analytically and gravimetrically determined protonation levels of the sample after SOCl_2 treatment were, within the experimental error, identical to the protonation level of polyaniline taken for drying. Carefully dried sample was then doped with FeCl_3 . The doping of $\text{PANI}(\text{HCl})_{0.43}$ was carried out in the same manner as the doping of PANI base. However in this case, the molar ratio of FeCl_3 to PANI mer was 1:2 because only half of nitrogen atoms were available for complexation.

Elemental Analysis. All samples studied were subjected to elemental analysis. C, H, and N were determined by combustion analysis. Cl was determined using Hg^{2+} (mercurometric determination) after Pt-catalyzed combustion of the sample in an oxygen atmosphere. Fe was determined by atomic absorption on previously mineralized samples.

Spectroscopic Investigations. Mössbauer spectra of PANI base doped with FeCl_3 and $\text{PANI}(\text{HCl})_{0.43}$ doped with FeCl_3 were measured in the temperature range 4.2–275 K. The samples were loaded in a drybox into a tight polyamide container prior to the experiment and immediately transferred to the cryostat of the spectrometer. Typical thickness of the absorber was 5 mg/cm^2 of natural iron. Co(Rh) was used as a Mössbauer source. An α -Fe absorber operating at RT was used for the velocity calibration. The spectra were recorded in a constant acceleration mode and analyzed in a least-squares procedure by diagonalization of the Hamiltonian describing quadrupolar interactions.¹⁰ The isomer shift (IS) values are given with respect to α -Fe.

EPR spectra were measured at RT using an ER 200 X band Bruker spectrometer (9GHz) with 100 kHz modulation.

UV-vis-NIR spectra of FeCl_3 -doped PANI solutions and solid films were recorded in an atmosphere of dry argon using a Perkin-Elmer λ 900 spectrometer.

Results and Discussion

In the studies of FeCl_3 doping of polyaniline, one must first verify whether this reaction is purely acid-base in nature. In such a case, Fe should not change its oxidation state upon its insertion into the polymer matrix. Figure 1a shows ^{57}Fe Mössbauer spectrum of FeCl_3 -doped emeraldine base registered at 77 K. This spectrum can be deconvoluted into three doublets. Two internal doublets are characteristic of Fe(III) high-spin complexes, whereas the external one which accounts for ca. 8% of total intensity at 77 K can be attributed to the reduced form of iron and, more particularly, hydrated FeCl_2 .¹¹ Thus, in this case, the overwhelming majority of the dopant molecules interact with the polymer matrix via Lewis acid-base complexation. However, there exists a small fraction which participates in a redox reaction involving the oxidation of reduced fragments of polyaniline. It can be demon-

(6) Huang, W. S.; MacDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1784.

(7) Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* **1987**, 82, 2385.

(8) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Photoelectron Spectroscopy of Conductive Polymers*. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 3, p 121.

(9) Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. *Synth. Met.* **1988**, 24, 193.

(10) Tomala, K.; Czjzek, G.; Fink, J.; Schmidt, H. *Solid State Commun.* **1977**, 24, 857.

(11) Greenwood, N. N.; Gibbs, T. C. In *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971.

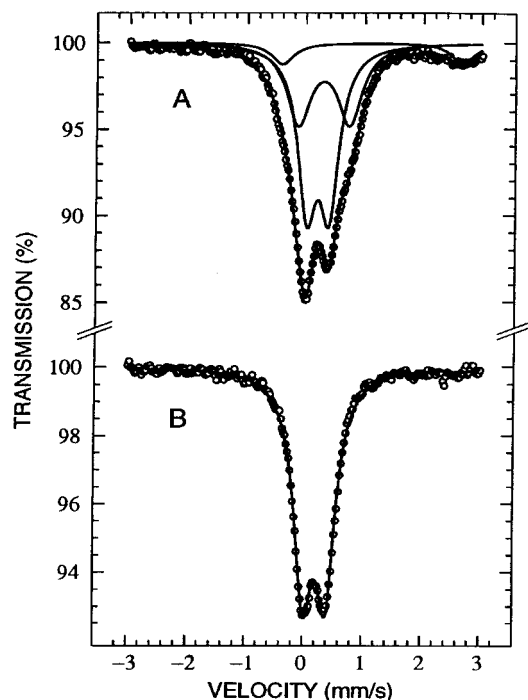


Figure 1. Mössbauer spectra registered at 77 K of (a) emeraldine doped with FeCl_3 and (b) emeraldine hydrochloride doped with FeCl_3 .

strated that this redox reaction is water-catalyzed because the contribution of Mössbauer lines attributed to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in the Mössbauer spectra of FeCl_3 -doped polyaniline increases upon the exposure of the polymer film to water vapor or upon addition of minute amounts of water to the doping solution. This redox side reaction is quickly terminated because FeCl_2 formed in this process becomes solvated with water molecules present in the system and quickly precipitates as a separate phase, removing in this manner water molecules from the polymer matrix. In addition, hydrolysis reaction may occur in the system. They are however of negligible importance because no hydrolysis products could be detected by Mössbauer spectroscopy. This is probably due to the fact that quick solvation of FeCl_2 with water molecules, followed by precipitation, impedes the hydrolysis.

Thus, to achieve 100% acid–base doping, one must carry out the reaction in a strictly anhydrous environment. In the case of a PANI base, it is extremely difficult because even extending pumping of PANI powder in a vacuum line with heating at 50 °C does not lead to the complete removal of water. We were unable to prepare FeCl_3 -doped PANI without hydrated FeCl_2 impurity. Depending on the sample studied, this contamination varied from 5 to 12% (at 77 K).

Mössbauer parameters of FeCl_3 -doped emeraldine are listed in Table 1. In the simplest interpretation, two coexisting Fe(III) doublets can be attributed to two nonequivalent complexing sites in the polymer matrix, namely, amine and imine nitrogens. To distinguish between these two sites, we have carried out the studies of FeCl_3 –Lewis acid base complexation of HCl-protonated emeraldine, i.e., PANI(HCl) $_{0.43}$. It is known that in the case of emeraldine protonation takes place preferentially on imine sites (vide supra). For this reason, in PANI(HCl) $_{0.43}$ two basic sites are available

Table 1. Mössbauer Parameters of Emeraldine Base and Emeraldine Hydrochloride Doped with FeCl_3 Measured at 78 K

sample		IS ^a (mm/s)	QS ^b (mm/s)	Θ_m (K)	Θ'_m (K)
(PANI)(FeCl_3) $_{0.87}$ - (NM) $_{0.87}$	ext. doublet	0.49(1) ^c	0.89(2)	172 (3)	126(5)
	int. doublet	0.32(1)	0.38(1)	114(3)	86(5)
(PANI)(HCl) $_{0.41}$ - (FeCl_3) $_{0.41}$ (NM) $_{0.27}$	one site	0.31(1)	0.38(1)	112(3)	79(5)

^a IS (isomer shift) relative to α -Fe. ^b QS (quadrupole shift) = $1/2 e^2 q Q$. ^c Errors are given in parentheses, in units corresponding to the last digit of quoted values.

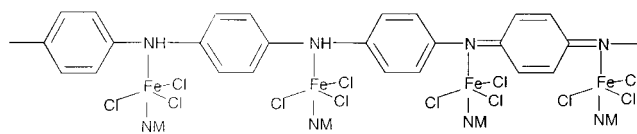
Table 2. Elemental Analysis of FeCl_3 -Doped Emeraldine and FeCl_3 -Doped Emeraldine Hydrochloride

	% C	% H	% N	% Cl	% Fe
emeraldine doped with FeCl_3					
calcd for (PANI)(FeCl_3) $_{0.87}$ (NM) $_{0.87}$ ^a	28.97	2.50	9.20	32.56	17.12
calcd for (PANI)(FeCl_3) $_{0.78}$ - ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) $_{0.09}$ (NM) $_{0.78}$	28.77	2.67	8.81	31.64	17.23
found (prep. 1)	28.50	2.58	8.39	31.16	17.14
found (prep. 2)	28.89	2.48	8.51	31.36	17.19
emeraldine chloride doped with FeCl_3					
calcd for (PANI)(HCl) $_{0.41}$ - (FeCl_3) $_{0.41}$ (NM) $_{0.27}$	39.90	3.03	9.43	30.87	12.17
found	40.18	3.13	9.22	30.60	12.21

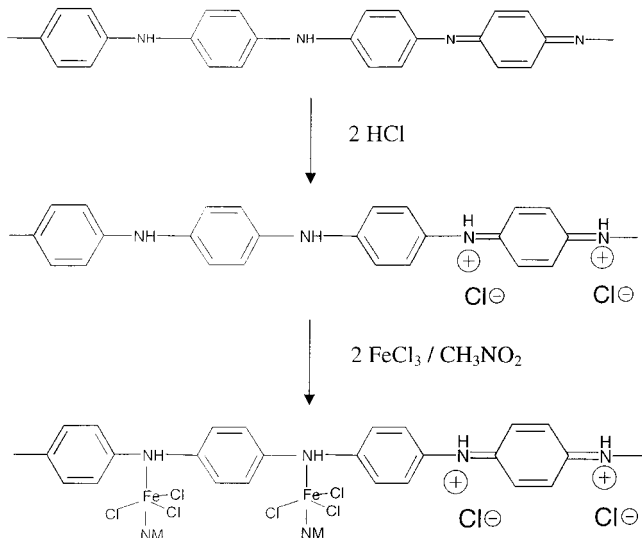
^a PANI denotes one polyaniline structural unit involving one ring and one nitrogen, i.e., $\text{C}_6\text{H}_4.5\text{N}$, since in the emeraldine base form there exist equal numbers of imine and amine nitrogens (4.5 is the average number of hydrogen atoms per structural unit). NM denotes the nitromethane molecule, CH_3NO_2 .

for Lewis acid complexation: amine nitrogens, which are strong bases, and Cl^- anions, which are weak bases. Imine sites being protonated are not available for FeCl_3 complexation. It is therefore evident that in this case the dopant will be complexed via amine nitrogens. A ^{57}Fe Mössbauer spectrum of PANI(HCl) $_{0.43}$ doped with FeCl_3 is presented in Figure 1b. This spectrum is much simpler than that characteristic of emeraldine base doped with FeCl_3 . First, the Fe(II) doublet is practically nonexistent; second, the external Fe(III) doublet has disappeared. The remaining doublet exhibits Mössbauer parameters practically identical to those of the internal Fe(III) doublet of FeCl_3 -doped emeraldine base (see Table 1). The conclusion is therefore straightforward: the internal doublet can be attributed to the complex formation via amine nitrogens, whereas the external one is attributable to the complexation on imine sites.

To establish the extent of Lewis acid doping of PANI base and PANI(HCl) $_{0.43}$, we have performed elemental analysis of the obtained compounds. The results are collected in Table 2. Following the results reported in Kulszewicz-Bajer et al.,⁴ we first expected that in the case of PANI base the doping will be complete, thus leading to the formula PANI(FeCl_3) $_{1.0}$ (NM) $_{1.0}$. In this formula, it is assumed that each dopant molecule entering the polymer matrix is solvated with one solvent molecule. Such assumption leads to a very poor agreement between the calculated and experimentally determined analytical data. The results of elemental analysis unequivocally show that only ca. 87% of sites available are complexed with a Lewis acid. In this case, the calculated and analytically determined contents of C, H, and Fe are in good agreement; however, N and Cl values are too high. Better fit of analytical data is obtained if one assumes, following Mössbauer spectro-

Scheme 1. Coexistence of Two Complexing Sites

NM: Nitromethane (CH_3NO_2)

Scheme 2. One Complexing Site

scopic results, that ca. 10% of iron is present in the form of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (see Table 2).

For the complexation of $\text{PANI}(\text{HCl})_{0.43}$ with FeCl_3 , it is not necessary to introduce the correction for the presence of hydrated FeCl_2 , which is consistent with Mössbauer spectra (no F(II) doublet in this case). The best fit is obtained for $\text{PANI}(\text{HCl})_{0.41}(\text{FeCl}_3)_{0.41}(\text{NM})_{0.27}$.

To summarize, elemental analysis shows 100% dopant solvation for PANI base doping and 70% dopant solvation for $\text{PANI}(\text{HCl})_{0.43}$ doping. The complexes formed upon doping can therefore be depicted as shown in Schemes 1 and 2. The above schematic picture implies the existence of a five-coordinated high-spin Fe(III) complex for both complexing sites in emeraldine. According to Reiff et al.,¹² pentacoordinated complexes of FeCl_3 with imines exhibit low values of isomer shift (less than 0.35 mm/s at ambient temperature) and the quadruple splitting value on the order of 0.5–0.9 mm/s. From the linear regression of $\text{IS} = f(T)$, the calculated value of the room temperature isomer shift is 0.34. Thus, Mössbauer parameters of the external doublet are characteristic of five-coordinated complexes of ferric chloride with imine type ligands. The room temperature value of IS for the internal doublet, calculated from the $\text{IS} = f(T)$ relation, is equal to 0.23. Thus, in this case, the five coordination of the complex is also expected.

For $\text{PANI}(\text{FeCl}_3)_{0.87}(\text{CH}_3\text{NO}_2)_{0.87}$, the intensity of the registered Mössbauer spectra is strongly temperature dependent. At temperatures close to room temperature, the absorption is very small, which indicates a significant mobility of the dopant in the polymer matrix. The recoil free fraction is related to the Debye temperature of the system θ and more precisely to the Mössbauer

lattice temperature θ_m , which is the lattice temperature as probed by the iron atom at a particular site. Because of two types of complexing sites in polyaniline, one may expect two different θ_m values because vibrational properties of iron at a particular site must depend on the type of bonding which the iron atom forms with the constituents of its coordination sphere (chlorine atoms, the polymer backbone, and nitromethane molecule). This must imply some modification of the Debye model which would take into account the influence of matrix on the vibrational properties of iron in the dopant molecules.

Within the high-temperature limit of the Debye model (T higher than $\theta_m/2$), the relationship between θ_m and the slope of the temperature dependence of the absorption $\ln A/dT$ can be expressed as follows:¹³

$$\Theta_m = \frac{E_\gamma}{c} \left[\frac{-3}{M_{\text{eff}} k (d \ln A/dT)} \right]^{1/2} \quad (1)$$

In a first approximation, one can use the mass of "bare" iron ion Fe^{3+} ($M_{\text{eff}} = 57$). This leads to the following formula for θ_m :

$$\Theta_m = 11.659 \left(-\frac{d \ln A}{dT} \right)^{-1/2} \quad (2)$$

However, in the case of doped polyaniline, we cannot use the mass of bare ferric cation because due to the complexation with the matrix the effective mass, M_{eff} , is higher than that of bare ferric cation. The correction for M_{eff} can be obtained from the slope of the temperature dependence of the isomer shift ($d\text{IS}/dT$) and more precisely from the second-order Doppler shift, which is given by the following equation:

$$\frac{d\text{IS}}{dT} = -\frac{3}{2} \frac{kE_\gamma}{2M_{\text{eff}}c^2} \quad (3)$$

In the case of ^{57}Fe , the combination of eqs 1 and 3 gives the following formula for Mössbauer lattice temperature corrected for M_{eff} :

$$\Theta_m = 432.03 \left[\frac{d\text{IS}/dT}{d \ln A/dT} \right]^{1/2} \quad (4)$$

Figures 2 and 3 show temperature dependence of the absorption and the isomer shift value for the two doublets. On the basis of these data, we have calculated Θ_m and Θ_m' for iron complexed at both complexing sites: amine and imine. The results are collected in Table 2. The calculated Mössbauer lattice temperatures are very low in the case of both complexing sites. These low Θ_m' values unequivocally indicate significant dopant mobility at temperatures close to room temperature.

The doping of polyaniline base with FeCl_3 results in a significant increase in the conductivity of this polymer which reaches its room temperature value of 0.2 S/cm for samples doped to saturation. Such a high value of conductivity implies high mobility of charge carriers. If charge carriers are also spin carriers, their motion can be probed by EPR spectroscopy. Several experimental results indicate that in protonated polyaniline charge

(12) Reiff, W. M.; Witten, J.; Takacs, J.; Zhang, J. H.; Toradi, C. C. *Hypersfine Interact.* **1990**, *56*, 1723.

(13) Herber, R. H.; Maeda, Y. *Physica* **1980**, *99B*, 352.

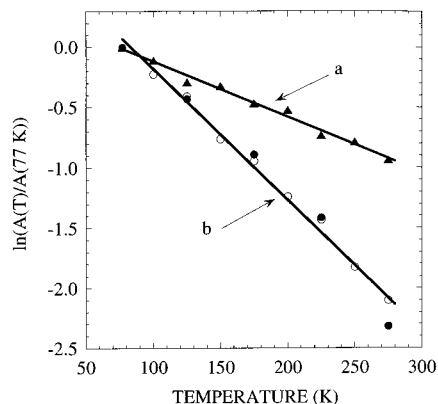


Figure 2. Temperature dependence of the recoil free fraction for external (a) and internal (b) doublets in FeCl_3 -doped emeraldine. The ordinate is the logarithm of the area normalized to the 77 K data point. In part b, the open circles correspond to emeraldine doped with FeCl_3 , whereas the full circles correspond to emeraldine hydrochloride doped with FeCl_3 .

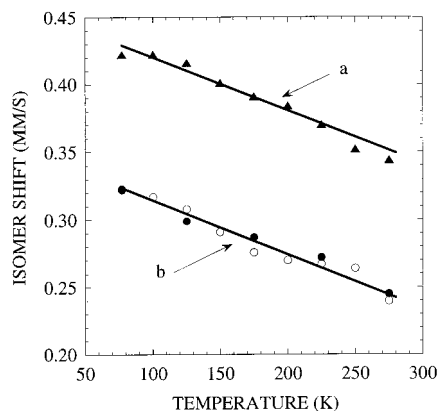


Figure 3. Temperature dependence of the isomer shift for external (a) and internal (b) doublets in FeCl_3 -doped emeraldine. In part b, the open circles correspond to emeraldine doped with FeCl_3 , whereas the full circles correspond to emeraldine hydrochloride doped with FeCl_3 .

carriers are of polaron type (see for example MacDiarmid et al.¹⁴ and Zuo et al.¹⁵). This is due to the stabilization of a poly(semiquinone radical) type structure, which in turn accounts for Pauli-like susceptibility observed in this material. In our previous papers,^{16,17} we have demonstrated that motionally narrowed polaron EPR line can be broadened by the interaction of mobile spins with fixed paramagnetic impurities present in the polymer matrix. This broadening is proportional to the concentration of the fixed spins and the mobility of the moving spins. Free spins associated with the polymer chains are also present in Lewis acid doped polyaniline. The origin of these spins is not clear at the present time. These may be residual spins always present in emeraldine base or spins created by Lewis acid doping as a result of charge redistribution. FeCl_3 molecules complexed on imine and amine sites play in turn the role of fixed paramagnetic impurities. Thus, if

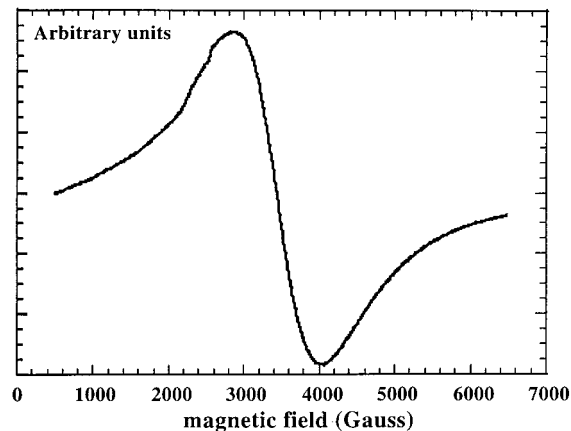


Figure 4. Room temperature EPR spectrum of emeraldine doped with FeCl_3 .

polyaniline spins in Lewis acid doped emeraldine are mobile, their line should be significantly broadened. Figure 4 shows room temperature EPR spectrum of FeCl_3 -doped polyaniline. The line centered at g around 2 is very broad ($\Delta H_{pp} \approx 1100$ G). This broadening is therefore consistent with the observed macroscopic conductivity of the sample.

Lewis acid doping with FeCl_3 also influences UV–vis–NIR spectrum of polyaniline. Before this problem is discussed, it is instructive to discuss spectral features of solutions and solid films of protonated polyaniline. The spectra of protonated polymer are strongly dependent on specific PANI–dopant–solvent interactions. Xia et al.¹⁸ distinguish two types of solution spectra: (i) Spectra of protonated PANI in inert solvents can be characterized by three localized absorption at 360, 440, and ca. 800 nm. The authors attribute these spectral features to three transitions characteristic of localized charge carriers (polarons). (ii) Spectra of protonated PANI in solvents capable of strong interactions with the dopant and the polymer (for example, the spectra of PANI doped with camphorsulfonic acid in *m*-cresol). In this case, only one absorption peak is observed in the UV part of the spectrum. In the NIR region, an increasing absorption tail can be seen which is attributed to charge carriers (polarons) delocalization. Films cast from such solutions are strong NIR absorbers and exhibit metallic type conductivity.

In our recent paper,¹⁹ we have demonstrated that the spectra discussed by Xia et al.¹⁸ represent two extreme cases and a large variety of “intermediate” spectra can be obtained by controlled modification of PANI–solvent–dopant interactions. Interestingly, the spectra of Lewis acid doped PANI, in their NIR part, strongly resemble those characteristic of metallic PANI despite much lower conductivity of this material. They are also strong NIR absorbers. As seen in Figure 5, the doping results in a total disappearance of the absorption at 640 nm characteristic of emeraldine base with simultaneous growth of an extremely broad absorption extending toward NIR with a maximum around 1700 nm (compare parts a and b of Figure 5). At the present state of art, it is difficult to speculate on the origin of this broadening.

(14) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285.

(15) Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1987**, *36*, 3475.

(16) Houz , E.; Nechtschein, M. *Phys. Rev. B* **1996**, *53*, 14309.

(17) Houz , E.; Nechtschein, M.; Pron, A. *Phys. Rev. B* **1997**, *5*, 12263.

(18) Xia, Y.; Wiesinger, J. M.; MacDiarmid, A. G.; Epstein, A. J. *Chem. Mater.* **1995**, *7*, 443.

(19) Rannou, P.; Gawlicka, A.; Berner, D.; Pron, A.; Nechtschein, M.; Djurado, D. *Macromolecules* **1998**, *31*, 3007.

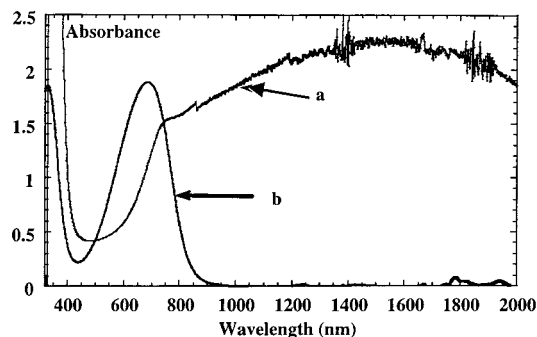


Figure 5. UV-vis-NIR spectrum of emeraldine doped with FeCl_3 in nitromethane (a) and emeraldine base in *N*-methylpyrrolidinone (b).

If the strong sensitivity of polyaniline chain conformation to secondary doping effects is taken into account, the observed broadening may originate from different

phenomena than in the case of the PANI-camphorsulfonic acid-*m*-cresol system.

Conclusions

To summarize, we have demonstrated that Lewis acid doping of emeraldine with FeCl_3 can be conveniently followed by ^{57}Fe Mössbauer spectroscopy which enables clear identification of both amine and imine complexing sites. FeCl_3 -doped polyaniline is conductive (0.2 S/cm) and exhibits interesting far-infrared absorbing properties.

Acknowledgment. I.K.B. acknowledges the Department of Chemistry of the Warsaw University of Technology for the grant promoting her habilitation research.

CM990485U