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Electron spin resonance spectroscopy and **electrical conductivity studies** on some polyaniline salts and their bases

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Four different polyaniline salts have been prepared by chemical oxidative polymerization of aniline with benzoyl peroxide as a novel oxidant employing inverse emulsion method at ambient temperature using different protonic acids (HCl, H₂SO₄, H₃PO₄ and sulphosalicylic acid). Their corresponding bases have been obtained by dedoping the salts with aqueous ammonium hydroxide. The polyaniline HCl salt exhibits the highest room temperature **conductivity** (2.31 S cm⁻¹). Temperature dependent EPR **studies** reveal Curie-Weiss and thermally activated paramagnetism for the polyaniline salts. No correlation between the magnetic properties and **conductivity** could be found.

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Fig. 1¾ Scheme of protonation and polaron formation in polyaniline

Among the family of conducting polymers, polyaniline and its derivatives have been the focus of attention due to their unique magnetic, optical and transport properties and high environmental stability¹. Different forms of polyaniline varying only in the degree of oxidation are known, among them the most important one being the emeraldine form containing equal amount of the oxidized and the reduced units in the polymer chain.

□ The **conductivity** of polyaniline could reversibly be controlled by both redox and protonation methods². A striking feature of polyaniline is that the insulating emeraldine base form of polyaniline can be rendered conducting on protonation by treatment with aqueous acids³ (Fig. 1). The **conductivity** increases by over six orders of magnitude. Protonated polyaniline is a highly disordered material. It is known to be inhomogeneously doped showing protonated regions called conductive islands, distributed sparsely in the bulk of the unprotonated matrix⁴.

□ Heavily doped conducting polymers are a class of quasi one-dimensional materials. It is generally assumed that the **electron** transport occurs primarily along the polymer chains⁵. **Conductivity**^{6,7}, optical reflectance⁸ and magneto **conductivity**^{9,10} of oriented "metallic" polymers have been found to be highly anisotropic. Models have been proposed based on the assumption that each polymer chain is an isolated one-dimensional conductor to account for many experimental observations¹¹⁻¹³.

□ **Electrically** conducting polymers contain a large number of unpaired **electrons** due to the defects in the polymer chains. These defects are caused mainly by the protonation induced **spin** unpairing mechanism, which causes a rearrangement in the structure of polyaniline having the following repeat unit,



where A^- denotes the counter anion and \cdot^+ an unpaired **spin** and a positive charge in the repeat unit^{11,14}. Significant increase in the paramagnetism arises chiefly due to the protonation of the polymer. Self-trapped carriers arising due to protonation of the conjugated polyaniline chains generate polarons and bipolarons. Two polarons under certain conditions couple to form a bipolaron. Polarons and bipolarons are localized excitations in non-degenerate conducting polymers. Bipolarons are **spinless** while polarons with **spin** of $\pm 1/2$ are EPR active.

□ EPR **spectroscopy** has been used to obtain information on **spin** localization and mobility and also to understand the interaction of the polaron **spin** with the environment¹⁵⁻¹⁸. **Studies** have revealed the highly paramagnetic nature of polyaniline with **spin** concentrations of about 10^{19} - 10^{21} **spins/g**¹⁹. The magnetic properties of polyaniline have been interpreted by Epstein and MacDiarmid²⁰ in two ways. One is concerned with the presence of two kinds of **spins**, namely, the Curie and Pauli **spins** as noted by the variation of magnetic susceptibility of polyaniline with temperature. The second concept is concerned with the presence of conducting

metallic islands in a lessconducting material in the bulk of polyaniline²¹. EPR spectra of chemically synthesized polyaniline show a single signal of either Gaussian or Lorentzian shape²¹. EPR spectra of electrochemically synthesized polyaniline have also been investigated^{22–24}. At higher doping levels, the spin concentration decreases due to pairing of polarons to bipolarons. Only at lower doping levels the identity between the spins and charge carriers, i.e. polarons, is valid as shown by the earlier EPR and conductivity studies. Spin susceptibility may decrease in some cases due to crossover from Curie to Pauli susceptibility^{25–28}.

□ Studies on temperature dependent EPR spectra and ambient temperature conductivity on some polyaniline salts and their bases are reported here. The polyaniline salts were synthesized using benzoyl peroxide as a novel organic oxidizing agent instead of conventional ammonium persulphate, with four different protonic acids, namely, hydrochloric (HCl), sulphuric (H₂SO₄), *o*-phosphoric (H₃PO₄) and sulphosalicylic (SSA) acids. The salts were converted to their corresponding bases using ammonium hydroxide. The polyaniline salts and bases have been characterized by electronic, FT-IR, FT-Raman and EPR spectroscopic techniques and also by conductivity studies.

Materials and Methods

Preparation of polyaniline salts and bases

□ Sodium lauryl sulphate in 50 ml of water (0.1 M) was added to a solution of benzoyl peroxide (0.2 M) in chloroform with stirring to obtain a milky white emulsion. Aniline (Merck) (0.1 M) was added to it followed by the dropwise addition of 100 ml of an aqueous solution of the dopant acid (HCl/H₂SO₄/H₃PO₄/sulphosalicylic acid) over a period of ½ h. As the reaction proceeded, the colourless emulsion turned green. The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. The dark green polyaniline solution in chloroform was treated with anhydrous sodium sulphate to remove the excess of water. The viscous organic solution was then added to 1.5 l of acetone in order to break the emulsion. The precipitated polyaniline salt was recovered by filtration as a dark green powder. It was washed with acetone and dried in vacuum for 36 h.

□ Part of the polyaniline salt synthesized was converted into the emeraldine base by overnight treatment with 0.5 M NH₄OH. The base obtained was filtered, washed with 0.5 M NH₄OH and dried in vacuum for 36 h.

Physical measurements

□ The dc conductivity of the samples was measured at ambient temperature using the four probe method (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50 kN/m². The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Keithley model 195A digital voltammeter is less than 2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample. The error in measuring the length and area of the pellet using Vernier calipers is 2–3%. The error in the conductivity value is expected to be < 3%.

Table 1—Absorption maxima for the polyaniline salts and their bases in DMSO

Polyaniline	UV-visible spectra (λ , nm)			
Pani-HCl salt	326	433	630	820
Pani-H ₃ PO ₄ salt	332	436	625	–
Pani-H ₂ SO ₄ salt	330	435	621	840
Pani-SSA salt	330	440	635	830
Pani-HCl base	330	–	625	–
Pani-H ₃ PO ₄ base	327	–	632	–
Pani-H ₂ SO ₄ base	320	–	624	–
Pani-SSA base	325	–	625	–

□ EPR spectra were recorded using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated to remove the moisture before recording the spectrum. The spectra were recorded at

different temperatures from room temperature to 200 °C at regular intervals. To obtain the g value and spin concentration, the EPR spectra of the sample and charred dextrose as a standard^{29,30} were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), field set (3280 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s) and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of polyaniline with that of charred dextrose. The calculated areas are likely to be within 5% of the true value^{29,30}.

□ The UV-visible absorption spectra of the samples in dimethylsulphoxide (DMSO) were measured using a Hitachi U-3000 spectrophotometer. FT-IR spectra were recorded with a Bruker Equinox 55 instrument by the KBr pellet technique. FT Raman spectra were obtained with a Bruker RFS100/S spectrometer using Nd³⁺: YAG laser with 30-40 mW power at the sample.

Results and Discussion

Absorption spectra

□ Table 1 gives the absorption maxima for the polyaniline **salts and bases in DMSO solution.**

As representative of the systems, the absorption spectra of polyaniline-sulphosalicylic acid salt and its base are given in Fig. 2. The spectrum of the polyaniline base exhibits two bands near 325 and 625 nm, whereas that of the salt shows four bands around 330, 440, 630 and 825 nm. The electronic absorption spectrum thus helps to detect the presence or otherwise of the polyaniline salt and its base.

□ The 325 nm absorption band is assigned to the p-p* transition of the phenyl rings. The absorption at 620 nm is attributed to the exciton transition (n-π*) from the HOMO of the benzenoid ring (non-bonding nitrogen lone pair) to the LUMO (π*) of the quinoid ring. The bands around 430 and 830 nm observed in the salts have been assigned as due to the polaron transition³¹. The absorption spectra of doped polyaniline (Table 1) exhibit bands at 840 and 440 nm demonstrating the presence of the salt form of polyaniline.

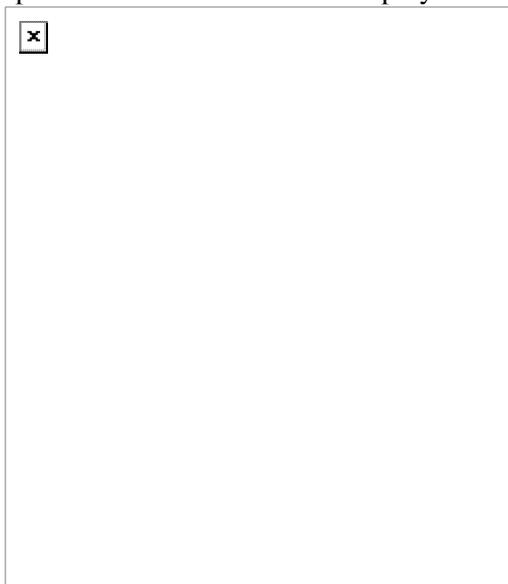


Fig. 2 ^{3/4} Electronic absorption spectra of (a) Pani-SSA salt and (b) its base

FT-IR and FT Raman spectra

□ The FT-IR spectra of polyaniline HCl salt and its base are given in Fig. 3. Changes in the infrared spectrum of the emeraldine base on protonation to the salt form may be expected due to changes in the dihedral angle between adjacent phenyl rings and the changes in the electronic structure. The doping of polyaniline leads to the formation of -Q=N⁺H- groups. A positive charge on the polymer chain may lead to an increase in the dipole

moment of the molecule, consequently resulting in increased intensity of the IR bands³². Most of the bands of the base are shifted towards lower frequencies in the spectra of the polyaniline salts due to the conversion of the quinoid rings to the benzenoid form. The bands at 1294 and 1234 cm^{-1} in the spectrum of the salt correspond to N-H bending and asymmetric C-N stretching mode of the benzenoid ring respectively. The band at 1573 cm^{-1} in the salt spectrum is assigned to the C=C ring stretching vibration. The band at 1475 cm^{-1} corresponds to the C-N stretching mode of the quinoid ring, which decreases in intensity on protonation of polyaniline by the dopant. In the IR spectrum of the salt, a band of medium intensity appears near 875 cm^{-1} , which is absent in the spectrum of the base. It is assigned to the ring-breathing mode of the quinoid group. A medium intensity band at 3230 cm^{-1} is assigned to the NH stretching mode. The presence of SO_3^- and -COOH groups is shown by the appearance in the spectrum of the salt doped with sulphosalicylic acid of bands around 570 and 1693 cm^{-1} arising from the degenerate bending mode of the SO_3^- group and carbonyl stretching respectively.

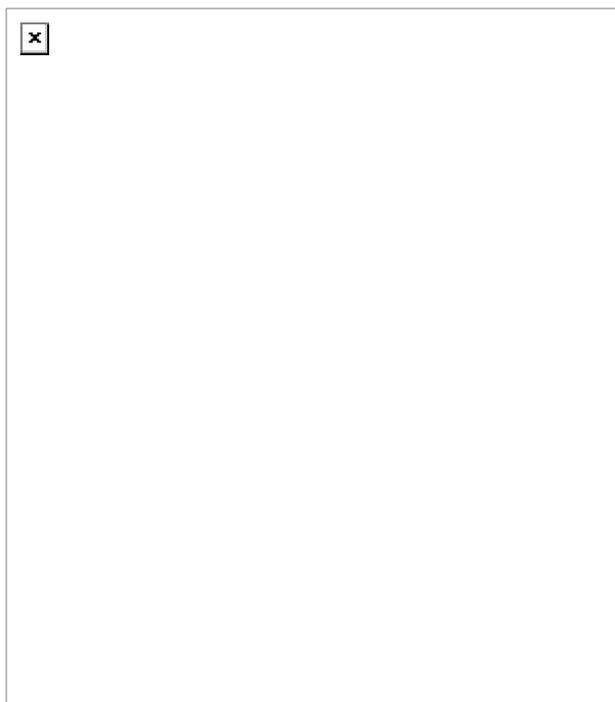


Fig. 3³ FT-IR spectra of (a) Pani-HCl salt and (b) its base

□ The Raman spectrum of polyaniline base has an intense band near 1500 cm^{-1} assigned chiefly to the benzenoid C-C ring stretching vibration and a band near 1600 cm^{-1} attributed to the quinoid C=C stretching mode of the polymer chain. The bands at 1598, 1508 and 1376 cm^{-1} are strengthened and new bands appear on the high/low frequency side for each of these bands in the spectra of the polyaniline salts. Several new less intense bands also appear in the Raman spectra of the salts. The 1328 cm^{-1} band in the salt is assigned to the C-C stretching mode of the quinoid ring. Due to differences in the conformation of the polymer and the extent of doping, the frequency of the C-C stretching vibration varies. The C-C bond is strengthened in the protonation induced polaron lattice. In particular, the Raman band at 1173 cm^{-1} assignable to the out of plane -CH bending, which is of weak to medium intensity, appears upon doping with dramatically enhanced intensity as the strongest band in the spectrum and its intensity increases with protonation. It can be assigned to Q=N⁺H structure which is formed on protonation.

Room temperature conductivity

□ The **electrical conductivity** of the polyaniline salts and their bases is presented in Table 2. The **conductivity** of Pani-HCl salt is the highest

(2.31 S cm^{-1}), and that of Pani – H_3PO_4 salt the lowest ($7.33 \times 10^{-2} \text{ S cm}^{-1}$). The **conductivity** of polyaniline base (10^{-9} - $10^{-10} \text{ S cm}^{-1}$) is much lower than that of the corresponding salt.

Roomtemperature EPR spectra

Table 2—EPR parameters for some polyanilinesalts and their bases measured at 298 K

System	Conductivity (S cm^{-1})	g value	Line- width (G)	Spin conc. (spins g^{-1})	Skin depth δ (m)	$\lambda = \theta/\delta$ ($\theta = 3 \times 10^{-3} \text{ m}$)
Salt						
Pani-HCl	2.31	2.0005	5.75	7.6290×10^{19}	3.4840×10^{-4}	8.6108
Pani- H_3PO_4	7.33×10^{-2}	2.0018	2.25	3.2370×10^{20}	1.9541×10^{-3}	1.5352
Pani- H_2SO_4	1.48	2.0012	2.75	2.6003×10^{20}	4.3473×10^{-4}	6.9008
Pani-SSA	5.90×10^{-1}	2.0025	2.25	3.1872×10^{20}	6.8876×10^{-4}	4.3557
Base						
Pani-HCl	2.00×10^{-9}	2.0011	11.00	6.3515×10^{18}	11.8299	2.5359×10^{-4}
Pani- H_3PO_4	2.99×10^{-10}	2.0023	10.25	9.0043×10^{18}	30.5752	9.8119×10^{-5}
Pani- H_2SO_4	8.16×10^{-10}	2.0011	12.50	1.0957×10^{18}	18.5236	1.6196×10^{-4}
Pani-SSA	5.24×10^{-10}	2.0011	9.50	4.9766×10^{18}	23.1048	1.2984×10^{-4}

□ Ambient temperature EPR parameters of polyanilinesalts and their bases are given in Table 2. The g value and the A/B ratio (thatis, the ratio of the area of the positive to the negative peak) do not revealunambiguously the nature of the polymer as to whether it is a salt or a base.The actual differentiation between the salt and the base is provided by the**spin** concentration and linewidth (ΔH). For a typical polyaniline salt, the **spin**concentration is around $10^{20} \text{ spins g}^{-1}$ and the value of DH issmaller, 2.0-3.0 G. On the other hand, for the base, the **spin** concentration islower, about $10^{18} \text{ spins g}^{-1}$ and the value of DH isgreater, about 8.0-12.0 G²⁴.

□ The g value of the polyaniline salts and their baseslies in a very narrow range 2.0008-2.0025. It indicates that the radical**electron spin** is localized on or near the nitrogen atom and on the psystem of the polyenes and aromatics²⁸. Ashift in the g value of at least 10^{-3} occurs when the radical **spin**is localized on or near the heteroatom .

□ In the EPR spectra of the polyaniline salts theobserved linewidth ranges from 2.25 to 5.75 G. The smaller linewidthsuggests mobility of the **spins** and there may also be strong exchange coupling.The observed linewidth for the corresponding polyaniline bases is greater, ~9.50 and 12.50 G.

□ The **spin** concentration of the polyaniline saltsvaries from 7.6×10^{19} to $3.23 \times 10^{20} \text{ spins g}^{-1}$ while that of the polyaniline bases is lower, $\sim 10^{18} \text{ spins g}^{-1}$. When polyaniline is doped witha protonic acid, the quinone imine nitrogens are protonated first formingbipolarons which are EPR inactive. An internal redoxmechanism converts the bipolarons formed on protonation into two polarons whichmigrate successively to reduce the Coulombic repulsions²¹. A decrease in the **spin** concentration in the base is attributed to the formationof bipolarons by **spin** pairing mechanism.

□ The EPR spectra of the polyaniline salts and theirbases exhibit a single signal without hyperfine splitting. The calculated skinddepth for the polyaniline salts and their bases is given in Table 2. The skinddepth δ is defined as the depth at which the current decays to $1/e$ ($= 0.369$) of its valueat the surface. It is given by the relation,

$$\delta = (\mu_0 \sigma \nu)^{-1/2} \text{ m} \quad \dots \square (1)$$

where μ_0 denotes the permeability of vacuum ($4\pi \times 10^{-7} \text{ Hm}^{-1}$), σ , the**electrical conductivity** (S m^{-1}) and ν the microwave frequency($9.05 \times 10^9 \text{ Hz}$)³². The calculated value of δ for the polyaniline saltsis of the order of 10^{-4} m which is greater than that of a goodconductor such as copper which has a value of $6.6 \times 10^{-7} \text{ m}$ at atypical EPR frequency. In a good conductor, the **conductivity** is very high andno free charges are present. Free charges generated in a good conductor move tothe surface with a time constant ϵ/σ (ϵ = permittivity and σ

=conductivity), which is extremely small. For the bases, however, the value of χ varies from 11.83 to 30.58 m (Table 2) which is typical of an insulator. For thin samples, the absorption curve is symmetrical and the line shape is Lorentzian since no Dysonian effect is expected³³. The characteristic effect of electron diffusion is to change the shape of the EPR signal rather than to broaden it.

Variable temperature EPR spectra

Temperature dependent EPR studies carried out on polyaniline salts and their bases have shown the g value and the A/B ratio to be temperature independent. However, the linewidth (ΔH) and the spin concentration vary. The behaviour of both Pani-H₂SO₄ (Fig. 4a) and Pani-SSA salts is similar i.e. ΔH decreases up to 353 K and then increases with temperature. For Pani-H₃PO₄ salt, ΔH is nearly constant (2.25G) up to 403 K and then increases with temperature up to 473 K. On the other hand, Pani-HCl salt shows a decrease in ΔH with rise in temperature. If the hopping rate for the spins is faster than the relaxation time (inverse of EPR time scale), the spins would experience an averaged magnetic environment leading to narrowing of the EPR line profile³⁴. Both Pani-H₃PO₄ and Pani-H₂SO₄ bases show a similar trend, that is, ΔH decreases sharply up to 353 and 440 K respectively, then increases with temperature. However, Pani-HCl base shows a steady decrease in ΔH from room temperature up to 473 K (Fig. 4b) and Pani-SSA base too shows a similar trend as the Pani-HCl base. For Pani-HCl salt, Wang *et al.*¹⁷ have reported that at $T > 100-200$ K, ΔH increases with temperature while at lower temperatures, ΔH decreases with increase in temperature and a minimum occurs between 150 and 200 K.

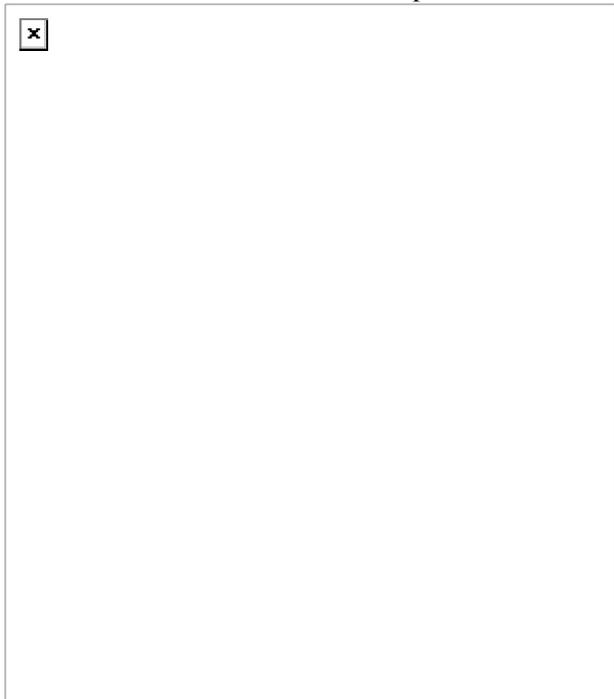


Fig. 4 Temperature dependence of spin concentration (spins g⁻¹) of (a) Pani-H₃PO₄ salt, (b) Pani-HCl base and (c) Pani-HCl salt

The spin concentrations of polyaniline salts and bases under investigation also show different variations with temperature.

- i) The spin concentration of Pani-H₃PO₄ (Fig. 5a), Pani-H₂SO₄, and Pani-SSA salts decreases with temperature indicating para-magnetism of the Curie-Weiss type.



Fig. 5³ EPR linewidth of (a) Pani-H₂SO₄ salt and (b) Pani-HCl base as a function of temperature

- ii) The bases of Pani-SSA, Pani-H₃PO₄ and Pani-HCl show enhanced **spin** concentration with temperature. This kind of behaviour is known as thermally activated paramagnetism (Fig. 5b). Polymers exhibiting strongly anti-ferro---magnetic interaction through super exchange generally show thermally activated paramagnetism³⁵.
 - iii) The Pani-HCl salt initially, up to 383 K, exhibits paramagnetism of the Curie-Weiss type, and from 383 K onwards it displays thermally activated paramagnetic behaviour (Fig. 5c), that is, the **spin** concentration increases with temperature. On the other hand, the Pani-H₂SO₄ base shows thermally activated paramagnetic behaviour up to 403 K and then as the temperature is raised further, it shows the Curie-Weiss type of paramagnetism, that is, the **spin** concentration decreases with temperature.
- The different variations in the **spin** concentration with temperature for different polyaniline salts may arise due to the different characteristics, such as the molecular shape, molecular motion and polarity of the counter ions^{29,36}. Thus the properties of polyaniline are influenced to some extent by the nature of the counteranions.

EPR properties of quasi -1D **spin** diffusion

□ The EPR parameters, namely, the g value, linewidth, line shape and **spin** concentration can serve as powerful probes of **spin** localization and dimensionality. Besides **spin**-lattice relaxation (T₁) and **spin-spin** relaxation (T₂), various other processes (T₂') cause broadening of the EPR **resonance** by shortening the lifetime of the **spin** state. The half linewidth ΔH_{1/2} is given by,

$$\Delta H_{1/2} = g^{-1}(1/T_2) = \gamma^{-1}(1/T_2' + 1/2T_1) \quad \dots \square (2)$$

where the gyromagnetic ratio $g = ge/2mc \approx 1.7588 \times 10^7 \text{ Hz G}$.

□ The **spin** dipole-dipole and hyperfine interactions chiefly contribute to 1/T₂' in the case of isolated **spins**. The **spin** dipole-dipole interaction ω_d is given by,

$$\omega_d = g H_d \quad \dots \square (3)$$

$$\text{where } H_d^2 = 5.1 (g \mu_B n)^2 S(S+1), \quad \dots \square (4)$$

□ Here n denotes the **spin** concentration, m_B is the Bohr magneton and $S = 1/2$

□ The hyperfine interaction ω_h can be obtained from the Eqs(5) and (6)

$$\omega_h = g H_h \quad \dots \square (5)$$

$$\text{and } H_h = (1/3) A^2 I (I+1) \quad \dots \square (6)$$

where A is the hyperfine splitting constant (for amine nitrogen NH^+ , $A=30$ G) and I is the nuclear **spin** (for ^{14}N , $I=1$).

□ On substituting the values, we obtain $H_h^2 = 600 G^2$.

□ If the **spins** are movable or if there is exchange interaction ω_e between the **spins**, narrowing of the signal occurs and if $\omega_e \gg \omega_d, \omega_h$, then,

$$1/T_2' = [(10/3) \omega_d^2 + \omega_h^2] / \omega_e \quad \dots \square (7)$$

□ The exchange interaction ω_e is given by $g H_e$ where γ defined above is the gyromagnetic ratio.

□ Equation (2) can be rewritten as,

$$\Delta H_{1/2} = g^{-1} (1/T_2') \quad \dots \square (8)$$

when the contribution from T_1 is negligible (as $T_1 \rightarrow 0$). Equation (7) can also be rewritten as,

$$H_e = \{(10/3) H_d^2 + H_h^2\} / \Delta H_{1/2} \quad \dots \square (9)$$

□ The values of $\Delta H_{1/2}$, H_d^2 , H_e and ω_e for the polyaniline salts and bases under investigation have been calculated. The exchange interaction rate is a function of

i) the interchain exchange integral t_{\perp} ,
 ii) mean free time τ for the **electron** moving along the chain and iii) the interchain mean free time t_1 . When ω_e is much smaller than $1/2 \tau$, localization occurs. It is observed that the value of ω_e is much smaller (10^8 to 10^9 Hz) than the scattering rate ($1/\tau \sim v_f/l_f \sim 10^{15}$ Hz where, l_f is the mean free path and v_f is the **electron** transverse velocity). The **electrons** are therefore in localized regions and hopping conduction mechanism is assumed in the amorphous region³⁷.

EPR and conductivity

- i) The **spin** concentration of Pani-HCl salt, 10^{19} **spins** g^{-1} , is an order of magnitude lower than that of Pani- H_3PO_4 salt, 10^{20} **spins** g^{-1} . However, the **conductivity** of the former is much higher (2.31 S cm^{-1}) than that of the latter (7.33×10^{-2} S cm^{-1}).
 - ii) The **spin** concentrations of Pani- H_2SO_4 and Pani- H_3PO_4 salts are comparable (10^{20} **spins** g^{-1}). However, the **conductivity** of the latter is nearly two orders of magnitude lower than that of the former (Table 2). These results do not lend support to the assumption that the EPR signal is due to the same species that carry the electric current as discussed above.
 - iii) For the polyaniline salts, the variation in EPR linewidth is small although there is a large variation in their **conductivity** (Table 2). The carrier mobility apparently is also not related to the linewidth.
- From the above observations, it may be said that the paramagnetic centers alone do not contribute to the **conductivity**, since no correlation seems to exist between **conductivity** and **spin** concentration. The observed thermally activated paramagnetism suggests the formation of bipolarons from polarons. A polaron that is present on a positively charged nitrogen, by polarization of the **electron** on the adjacent carbon atom, induces **spin** polarization in succession until an unpaired **electron** is encountered on a nitrogen atom. It leads to two unpaired **electrons** that are coupled antiferromagnetically. It involves the interaction of a number of polaron **spins** that are present along the polymer chain. The polarons or radical cations are EPR active. The presence of polarons in polyaniline salts and their bases is evident from the EPR **studies**. In polyaniline both polarons and bipolarons exist, while polarons are **spin** carriers, the charge carriers are polarons as well as bipolarons.

Similar observations have been made from **studies** on polypyrroles and poly(4,4'-methylenedianiline) ^{26,29}.

Conclusion

□ The EPR spectroscopic **studies** have revealed for the polyaniline salts of HCl, H₂SO₄, H₃PO₄ and sulphosalicylic acid paramagnetism of Curie-Weiss type. However, the bases display predominantly thermally activated paramagnetism. The EPR line shape is Lorentzian and Dysonian effect is not observed. In polyaniline the presence of both polarons and bipolarons is suggested from EPR **studies**. There appears to be no relationship between **conductivity** and **spin** concentration. Thus the charge transport cannot be explained solely in terms of the migration of the paramagnetic species. The **electrons** are present in a localized region and hopping conduction is assumed in the amorphous regions of polyaniline.

*Supplementary material available

□ Tables 3-6 listing the values of **spin** concentration, g factor, ΔH , H_d^2 , H_e and ω_e of the polyaniline salts and their bases are available from the authors.

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