Effect of dioxygen on ESR spectra of polyaniline

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The effect of dioxygen on the width of ESR lines of powders and films of polyaniline was studied at 15—300 K. It was found that the line broadening can decrease or increase, which corresponds to strong or weak exchange, respectively. For dry polyaniline powders and films, maximum broadening was observed at 240 K. The findings were explained by spin exchange during collisions of a mobile polaron with immobile O_2 molecules bound to the polymer. The values of exchange interaction between the O_2 molecule and the polaron and the mobility of the polarons along the polymer chain were found. The mobility of polarons along the polymer chains decreases in the presence of H_2O, and dioxygen predominantly adds to the imine N atom.

Key words: polyaniline, ESR, dioxygen, mobility of polarons.

The capability of dioxygen to reversibly broaden ESR lines of polyaniline without changing its conductivity has rather long been known.[1—5] This effect of dioxygen is much enhanced after pre-evacuation of the samples, and the broadening decreases ("relaxes") over time.[5—7] A similar effect of dioxygen has also been observed with polypyrrole.[8,9] The main specific features of the dioxygen effect on the ESR linewidth can be explained by a model according to which the paramagnetic O_2 molecule adds to a polymer, and the exchange interaction at the moment of collisions between spins of the immobile O_2 and the mobile polaron results in the broadening. The enhancement of the O_2 effect after pre-evacuation and "relaxation" are due to the competition of the O_2 and H_2O molecules for binding sites on the polymer.

The ESR method allows direct studies of polarons to be carried out. Polarons are paramagnetic charge carriers playing a key role in the physics of conducting polymers.

According to the quantitative theory of the dioxygen effect,[10] the broadening of the ESR line of polyaniline is described by the formula

$$\delta(\Delta\omega) = p\omega_{\text{hop}}C, \qquad (1)$$

where $\Delta\omega$ is the linewidth in rad s^{-1}, ω_{hop} is the frequency of polaron jumps, C is the concentration of sorbed oxygen (per aniline unit), and p is the probability of spin reorientation within the time of the polaron and O_2 molecule collision. If the time of spin-lattice relaxation of the electron spin of the O_2 molecule is longer than the collision time, the p value can be determined by the formula

$$p = \frac{16}{27}\,\frac{(9/4)J^2t^2}{1+(9/4)J^2t^2}, \qquad (2)$$

where J is the exchange interaction in rad s^{-1}, and t is the average time of collision of the O_2 with the polaron. Similar formulas have been derived for different cases.[11] The ω_{hop} and t values are related[10] by the correlation

$$t = L^2/\omega_{\text{hop}}, \qquad (3)$$

where L is the number of polyaniline units occupied by the polaron, usually being accepted as $L = 4$.

The existence of two situations of exchange, weak and strong, is an important consequence of formulas (1)—(3). For the weak exchange, $J^2t^2 \ll 1$, due to which $\delta(\Delta\omega) \sim 1/\omega_{\text{hop}}$; for the strong interaction, $J^2t^2 \gg 1$, hence, $\delta(\Delta\omega) \sim \omega_{\text{hop}}$.

Previously,[10] based on measurements of the broadening at room temperature and taking into account the published data on the mobility of polarons and the amount of dioxygen absorbed by polyaniline, it has been suggested that $p \approx 0.04$—0.4, *i.e.*, the situation is close to the strong exchange. However, this conclusion is based on several assumptions. Temperature measurements make it possible to determine[11] which situation takes place. The mobility of polarons ω_{hop} increases as the temperature increases. If the broadening increases with temperature increase, strong exchange takes place, and if the temperature decreases, weak exchange is observed.

In this work, we studied the temperature dependence (in the 15—300 K range) of the oxygen broadening for different polyaniline samples (either dry or in solutions).

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Experimental

Polyaniline samples PAN1 and PAN2 were prepared as follows. Polyaniline PAN1 was synthesized for 2 h at ~20 °C in water containing aniline (0.1 mol L^{-1}), $(NH_4)_2S_2O_8$ (0.08 mol L^{-1}), and $HClO_4$ (0.1 mol L^{-1}). PAN1 samples were studied either directly in the reaction mixture or after washing off (without drying) with different solvents. Polyaniline PAN2 was synthesized for 5 h at −5 °C in acetonitrile containing aniline (1 mol L) and $HClO_4$ (1 mol L^{-1}) with the gradual addition of $(NH_4)_2S_2O_8$ (1 mol L^{-1}); the precipitate was repeatedly washed off with acetonitrile, water, and 0.1 *M* $HClO_4$ (to obtain the salt of polyaniline) and dried at 40 °C. The PAN2 films cast from *N*-methylpyrrolidone possess a conductivity of ~1 S cm^{-1} (determined by the four-probe method).

ESR spectra were recorded on an SE/X-2544 radiospectrometer (Radiopan, Poland) equipped with a temperature unit for studies at temperatures >100 K and an attachment similar to that described previously[12] for work at temperatures of liquid helium. ESR spectra were recorded at sufficiently low values of the magnetic modulation amplitude and at UHF field power for which the distortion of the line shape is negligible. The linewidth ΔH was measured between the maxima of the first derivative.

To remove dioxygen, polyaniline samples were placed in thin-walled polyethylene tubes with an inner diameter of ~1 mm, which were blown with argon. Gases penetrated through the walls of the polyethylene tubes, and dioxygen was rather rapidly removed from the sample. Argon can be replaced by dioxygen in a similar way. The removal of dioxygen from polyaniline (2—3 h) was monitored by the ESR linewidth of polyaniline. The removal of dioxygen from the solvent (15—30 min) was monitored by the ESR linewidth of the nitroxyl radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxo (TEMPON), which was specially introduced into the reaction mixture or solution. In this case, the broadening ($\delta(\Delta H)$/mT) occurs due to exchange interaction between the spins of oxygen and nitroxyl at the moment of their collisions, and its change can be described by the formula[11]:

$$\delta(\Delta H) = \Delta H - \Delta H_0 = 5.6 \cdot 10^{-9} K_e C, \qquad (4)$$

where C is the concentration of dioxygen in mol L^{-1}, and K_e is the spin exchange constant. For dioxygen in water at room temperature, $K_e = 7.1 \cdot 10^9$ L mol^{-1} s^{-1}.[13] Knowing the K_e and $\delta(\Delta H)$ values, we can calculate the concentration of dioxygen.

Dioxygen was removed from films and powders by evacuation with a diffusion pump at a residual pressure of $\leq 10^{-4}$ Torr for 2 h. Times of dioxygen removal were chosen from the condition that the ESR linewidth remains unchanged with an accuracy to 0.001 mT at a longer removal.

Results and Discussion

The typical temperature dependences of the ESR linewidth of the PAN2 powder are presented in Fig. 1. The ESR line has the Lorentzian shape with a *g* factor of 2.0028. The following correlation between the ΔH and $\Delta\omega$ values is fulfilled for the Lorentzian line:

$$\Delta\omega = (\sqrt{3}/2)\gamma\Delta H, \qquad (5)$$

where γ is the electron gyromagnetic ratio ($1.77 \cdot 10^8$ mT^{-1} s^{-1}). The narrowest line is observed in a vacuum after 2-h evacuation at 10^{-4} Torr, and the linewidth (0.08 mT) is almost temperature-independent (see Fig. 1, curve *1*). The admission of air (curve *4*) or pure dioxygen at 1 atm (curve *5*) to the sample results in the broadening of the line approximately proportionally to the partial pressure of dioxygen. The maxima on curves *4* and *5* are explained by the transition from the weak exchange at high temperatures to the strong exchange at low temperatures. After the air admission, the linewidth relaxes during 2—3 h to that of the starting powder exposed to the air for a long time (curve *3*), which is explained by competition between the O_2 and H_2O molecules for the binding sites. The relaxation in pure dioxygen is slower due to a lower content of H_2O vapor in dioxygen. Admission of the saturated water vapor to the evacuated sample results in a weak broadening (see Fig. 1, curve *2*). The water was pre-deaerated by careful evacuation with a forevacuum pump; therefore, the broadening is not related to the presence of residual dioxygen. When air was admitted to the sample in the water vapor, the linewidths were close to those for the starting sample in the air. The introduction of dioxygen results in a noticeable decrease in the *g* factor of the PAN2 powder at room temperature from 2.0028 *in vacuo* to 2.0026 in dioxygen at 1 atm. According to the spin exchange theory,[11] an average *g* factor should be observed at sufficiently short times between collisions of

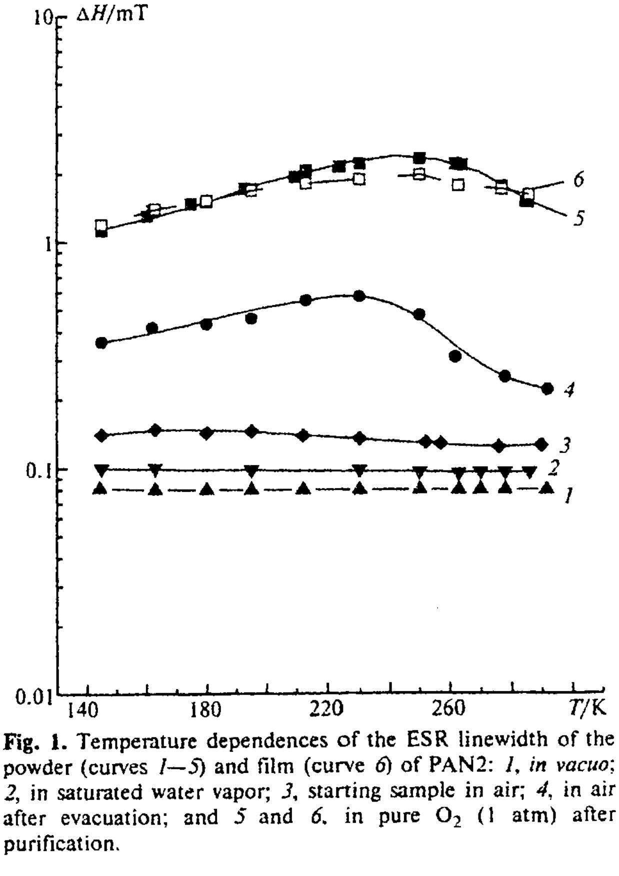

Fig. 1. Temperature dependences of the ESR linewidth of the powder (curves *1—5*) and film (curve *6*) of PAN2: *1*, *in vacuo*; *2*, in saturated water vapor; *3*, starting sample in air; *4*, in air after evacuation; and *5* and *6*, in pure O_2 (1 atm) after purification.

the paramagnetic centers with different *g* factors. The value of the *g* factor of O_2 added to polyaniline is unknown; however, the decrease in the *g* factor under O_2 action agrees with the lowered *g* factor of molecular O_2 in the liquid state: at 77 K dioxygen is condensed from the air to give a broad (~400 mT) line with a *g* factor of ~1.7.

The broadenings that appeared during the O_2 admission to the evacuated PAN2 film (see Fig. 1, curve *6*) are close to those for the PAN2 powder.

In addition to dry films and powders, we studied freshly prepared powders and precipitates of polyaniline synthesized in various solutions. For these samples, another mechanism is possible, which is due to collisions of mobile O_2 molecules that freely diffuse in the solution with mobile polarons, along with the above considered broadening due to collisions of mobile polarons with immobile O_2 molecules sorbed on the polyaniline molecule.

For PAN1 synthesized in an aqueous reaction medium and washed off with 0.1 *M* $HClO_4$, the ESR line is close to the Lorentzian line at all temperatures (Fig. 2). The temperature dependence for polyaniline in air can be explained as follows. When the temperature decreases from room to 270 K, the solution is divided into ice and liquid acid, and liquid $HClO_4$ with a higher content of O_2 covers the polyaniline molecules. The concentration of O_2 in this layer is elevated due to the displacement of O_2 from the ice. This results in a greater broadening by both the first and second mechanisms. The sharp decrease in the linewidth at 210 K can be explained by the fact that the second mechanism does not take place because of freezing of the acid. Sharp changes in the linewidth at 270 and 210 K are not accompained by change in the value of the second integral of the ESR spectrum, *i.e.*, the number of unpaired electrons remains unchanged.

To verify the assumption on the phase separation, we studied the temperature dependence of the ESR linewidth of a solution of the TEMPON nitroxyl (0.1 mol L^{-1}) in 0.1 *M* $HClO_4$. Freezing of this solution at 270 K in air results in the broadening of the central ESR line from 0.035 to 0.117 mT, whereas the broadening in argon is much smaller, from 0.028 to 0.042 mT. The change in the broadening in air is mainly due to the displacement of TEMPON and O_2 from the ice to the liquid phase containing $HClO_4$. In argon the broadening changes due to an increased viscosity of the liquid phase as compared to that of the solution before freezing.

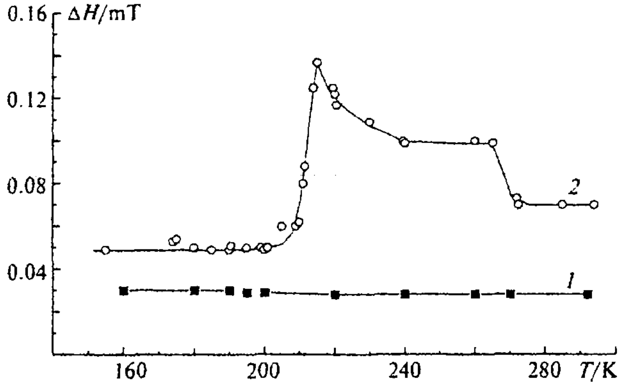

Fig. 2. Temperature dependence of the ESR linewidth of PAN1 in 0.1 *M* $HClO_4$ in argon (*1*) and air (*2*). PAN1 was synthesized in an aqueous reaction mixture and then washed off with 0.1 *M* $HClO_4$.

When the temperature decreases from 270 to 210 K, the correlation time of nitroxyl rotation (the methods of determining the correlation time τ_c have been described previously, see, *e.g.*, Ref. 14) increases from 10^{-10} to $>10^{-9}$ s, *i.e.*, the viscosity of the liquid phase gradually increases. Perhaps, the increase in the oxygen broadening in the 270—210 K range is related to an increase in the viscosity. For O_2 the efficiency of spin reorientation *p* increases[15] as the viscosity of the solution increases and amounts to 0.5 and 1.0 for viscosities of 1 and 4 cP, respectively. At temperatures <210 K, the rotation of the radical is sharply retarded: $\tau_c > 10^{-7}$.

The effect of O_2 on the ESR linewidth of PAN1 in 0.1 *M* $HClO_4$ is reversible. After the air—argon—air cycle, the temperature dependence of ΔH remains unchanged. Heating of this sample to 370 K also has no effect on the temperature dependence. If the PAN1 sample is washed with other solvents, different temperature dependences of the linewidths of the samples in the air are observed (Fig 3). For example, for PAN1 in water, no sharp decrease in ΔH at 210 K is observed, and the linewidth decreases with temperature decrease to lower than 270 K. In acetonitrile broadening jumps occur at 230 K (the freezing point of acetonitrile is 225 K) and 210 K, and the width increases as the temperature decreases <210 K. In argon the linewidth is much more narrow and monotonically increases with

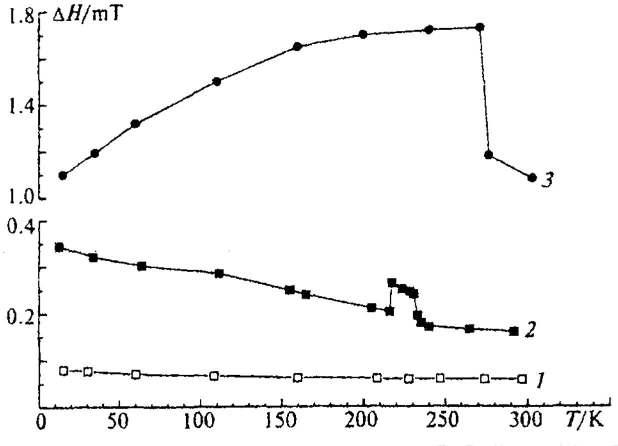

Fig. 3. Temperature dependences of the ESR linewidth of PAN1 in water in argon (*1*), in acetonitrile in air (*2*), and in water in air (*3*). PAN1 was synthesized in an aqueous reaction medium and then washed off with water or acetonitrile.

temperature decrease. For example, in water ΔH is equal to 0.047 and 0.080 mT at 290 and 14 K, respectively; close values were obtained in acetonitrile.

The data in Fig. 3 indicate that the solvent nature substantially affects the Jt value. In a wide temperature range from room to helium temperature, the strong exchange takes place in water and the weak exchange is observed in acetonitrile. The Jt product can vary due to both a change in the mobility of polarons $\omega_{\text{hop}} \sim 1/t$ and the exchange interaction J. The J value should depend on the site of addition of O_2 to polyaniline. The O_2 molecule can add[7] to either counteranions (in our case, ClO_4^-) or the amine N atom ($-NH^+-$).

Until the present time, we considered entirely doped polyaniline samples containing only amine N atoms. The imine $=N-$ atom appears when the degree of doping decreases. We studied the influence of the degree of doping of PAN1 on the oxygen effect to determine to which of the N atoms the O_2 affinity is higher. A decrease in the degree of doping was judged from an increase in the ESR linewidth, because an increase in the fraction of the imine N atom distorts the conjugation in the polymer chain. The degree of doping was changed by dilution of the reaction mixture (after the end of the synthesis) with water by 4, 16, and 48 times, and the linewidth in argon ΔH_0 increased from 30 to 103 μT (Table 1). The ratio of broadenings of the ESR lines of polyaniline and TEMPON nitroxyl in the same solution was measured to take into account the change in the O_2 concentration in a solution with this dilution. The data obtained show that the oxygen broadening of the ESR lines of polyaniline increases as dilution increases, *i.e.*, in water the O_2 molecules predominantly add to the imine N atom of polyaniline.

The broadening of the lines of PAN2 in the presence of O_2 is much less than that of PAN1 (see Table 1). We previously have shown[16] that the ESR lines of PAN1 and PAN2 are broadened in different ways by other paramagnetic ions, $Fe(CN)_6^{3-}$ and Co^{2+}. In PAN2 the paramagnetic centers are heterogeneous and less accessible for collisions with the paramagnetic ions that freely diffuse in the solution. When PAN2 is immersed into an aqueous solution, the ESR line becomes asymmetric, which is characterized by the ratio A/B of amplitudes of the deviations of the first derivative of the ESR signal from the reference line. Asymmetry of the signal is due to the high conductivity of this film at a frequency of the UHF radiation and, as a consequence, to the small thickness of the skin layer.[17] Analysis of the temperature dependence of A/B showed[18] that the molecular motions of the polyaniline segments are substantial for its conductivity, and when the solutions are frozen, the A/B value becomes equal to 1.

The temperature dependences of A/B and ΔH for PAN2 in aqueous solutions in air are presented in Fig. 4. For PAN2 in water and in 1 M HCl, freezing of the solutions at ~260 K is accompanied by a sharp increase in the linewidth due to the displacement of O_2 from the ice and a sharp decrease in A/B due to the retardation of the molecular polyaniline chains. After removal of dioxygen, the A/B values remain unchanged (*i.e.*, O_2 has no effect on the conductivity of polyaniline), and the linewidths decrease and are virtually temperature-independent. Unlike PAN1 (see Fig. 2), for PAN2 in 0.1 M $HClO_4$, freezing of the solution is not accompanied by sharp changes in A/B and ΔH. This distinction between PAN1 and PAN2 has no explanation yet.

It is seen in Fig. 4 that the strong exchange occurs for PAN2 in water, and the transition from the weak to strong interaction is observed in aqueous solutions of $HClO_4$ and HCl with temperature decrease.

Thus, analysis of the temperature dependences makes it possible to determine the type of exchange interaction

Table 1. Effect of air dioxygen on the linewidth in the ESR spectra of polyaniline and nitroxyl radical at ~20 °C

Sample	Medium	ΔH_0[a]	$\delta(\Delta H)$[b]	$\delta(\Delta H_0)_{\text{PAN}}$ / $\delta(\Delta H_0)_{\text{TEMPON}}$
		μT		
PAN1	0.1 M $HClO_4$	22	50	6.2
	I[c]	30	25	2.5
	II[d] (1 : 4)	35	30	3.0
	II (1 : 16)	71	47	4.7
	II (1 : 48)	103	90	9.0
TEMPON	0.1 M $HClO_4$	31	8	—
	I	31	10	—
	H_2O	28	13	—
PAN2	H_2O	176	13	1.0

[a] ΔH_0 is the ESR linewidth of the samples in argon.
[b] $\delta(\Delta H)$ is the line broadening in air.
[c] The ESR spectra of polyaniline were recorded after the end of the synthesis in an aqueous medium without washing off.
[d] After the end of the synthesis, water was added to the reaction medium, and the degree of dilution of the reaction mixture with water is given in parentheses.

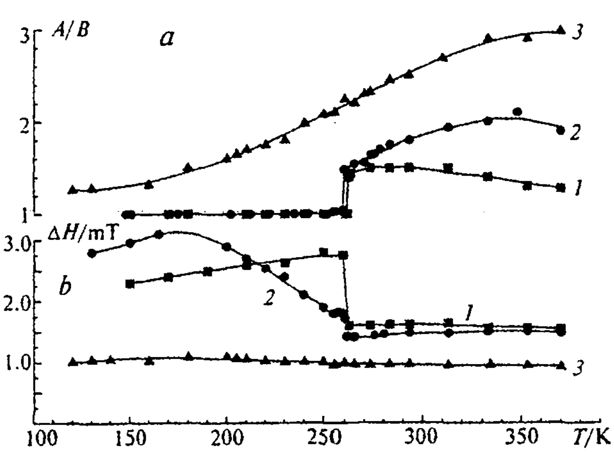

Fig. 4. Temperature dependences of the asymmetry parameter A/B (*a*) and ESR linewidth (*b*) of PAN2 in various solutions in air: in water (*1*), 1 M HCl (*2*), and 0.1 M $HClO_4$ (*3*).

(weak or strong), which is important for revealing a correlation between the oxygen broadening and the conductivity of the sample. For example, it has been found[19] that at room temperature during aging of the polypyrrole film its conductivity decreased, and the ESR linewidth decreased. A great linewidth for the freshly prepared sample was explained by collisions of polarons with admixtures of iron ions. The line can narrow with a decrease in the film conductivity only in the case of strong exchange. It has lately been shown[8] that the dioxygen effect for the polypyrrole film is highest at 15 K, *i.e.*, the weak exchange occurs at room temperature, and other explanations of the line narrowing during film aging should be found.

The maximum of oxygen broadening is observed at ~240 K (see Fig. 1, curves *5* and *6*) for dry powders and films of PAN2 with temperature decrease. The observation of this maximum allows the J and ω_{hop} values to be calculated. The formula for the oxygen broadening follows from Eqs. (1)—(3) and (5):

$$\delta(\Delta H) = 2.8 \cdot 10^{-13} L^2 J C x / (1 + x^2), \qquad (6)$$

where ΔH/mT is the broadening of the ESR line by O_2, L is the degree of delocalization of a polaron in the polyaniline units (usually $L = 4$), J/rad s^{-1} is the exchange interaction between O_2 and the polaron, C is the concentration of O_2 per polyaniline unit, and $x = 3/2J\tau$. According to studies,[20] for the O_2 pressure of 1 atm, C amounts to 0.005 of the number of O_2 molecules per polyaniline unit. The data obtained[20] do not allow one to distinguish the O_2 molecules sorbed and dissolved in polyaniline. Then let us assume that all O_2 was sorbed on polyaniline. In formula (6), only x depends on the temperature; therefore, the observation of a maximum on the temperature dependence of $\delta(\Delta H)$ makes it possible to determine x as a function of the temperature and calculate J. It follows from the data for the PAN2 powder and film (see Fig. 1, curves *5* and *6*) that $J = 1 \cdot 10^{12}$ rad s^{-1}, and the $\omega_{\text{hop}} \cdot 10^{-12}$ value increases with temperature increase and amounts to 5.8, 24, and 67 at 145, 240, and 285 K, respectively. The value $J = 1 \cdot 10^{12}$ rad s^{-1} ranges in the limits characteristic of the spin exchange between the nitroxyls and paramagnetic ions[11] (10^{10}—10^{13} rad s^{-1}), and the ω_{hop} values presented above are close by an order of magnitude to ω_{hop} published previously.[10,21] Formula (6) gives two arrays of x values, either increasing or decreasing with temperature increase. The ω_{hop} values mentioned were obtained under the assumption that the mobility of polarons ω_{hop} increased with temperature increase. However, the ω_{hop} values determined previously[21] decrease as the temperature increases.

Dioxygen can form weak donor-acceptor bonds with molecules of organic compounds.[22] The formation of these complexes is indicated by the paramagnetic shifts and luminescence of the organic molecules. In particular, a substantial paramagnetic shift was observed for protons of the amino groups in aniline and pyrrolidone. The equilibrium constants of the dioxygen complexes are low (10^{-2} L mol^{-1}). A close equilibrium constant for polyaniline (0.1 L mol^{-1}) can be estimated from the data on the amount of O_2 absorbed by polyaniline.[20] It is of interest that for the PAN2 powder, the maximum on the temperature dependence of ΔH is shifted toward high temperatures (see Fig. 1, curves *4* and *5*) with an increase in the partial pressure of O_2. Perhaps, this is related to the fact that O_2 adds to different sites of the polyaniline molecule with different binding constants and different J.

The nature of a solvent substantially affects the mobility of polarons. For example, the strong exchange is observed for PAN1 and PAN2 in water at 15—270 K (*i.e.*, the mobility of polarons is low), whereas for PAN1 in acetonitrile, the weak exchange is observed. The high mobility of polarons is due to the possibility of their isoenergetic jumps; perhaps, water violates this isoenergetic character because of the formation of hydrogen bonds with polyaniline. The broadening of the ESR line of PAN2 in the water vapor (see Fig. 1, curve *2*) also indicates a decrease in the mobility of polarons at room temperature under the action of H_2O. According to modern concepts, these are the jumps of polarons along the chain which result in the averaging of HFC from protons and N nuclei and the narrowing of the ESR line.

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