Ionomer-like behaviour of protonated polyaniline: effect of ionic strength on the optical spectra

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The absorbances of polyaniline (PAni) at 850 nm due to the electronic transition from a polaron band and at 130 cm^{-1} due to vibrational excitation of the hydrogen bond are observed to change non-linearly with the degree of protonation. The extent of non-linearity for these changes is dependent on the ionic strength of the protonating medium. The effect of ionic strength on the bands originating from the two different types of transitions (electronic and vibrational) are found to be similar. A model has been proposed relating PAni with ionomers to account for the observations. This also provides an explanation for the formation of metallic islands in the polymer. It seems that the distribution of the dopants in the polymer matrix and the interchain interactions have a combined influence on the electronic structure of protonated PAni.

Properties of conducting polymers are known to be dependent on the type of dopant counter ion, the molecular environment of the polymer and other factors that determine the intermolecular interactions in the system. Polyaniline (PAni) has been found to be the most interesting polymer in this respect.[1] Apart from being dependent on the protonation of the polymer, known as acid doping,[2] the electrical conductivity, optical properties and other electronic properties of PAni are highly sensitive to factors such as the nature of the dopant, the solvent from which the PAni film is cast, and the presence of any additive.[1,3] The change in the properties may be so great that the process of modification of conductivity and other properties by using appropriate additives has been termed secondary doping[3] and its mechanism has been related to the structure of the polymer on a scale larger than the molecular level (*e.g.* conformation of the polymer chain, crystallinity, *etc.*).[3] Other larger scale features reported are the metallic islands[4] in protonated PAni and physical cross-linking of the polymer chains.[5] Spectroscopic studies in the near-IR region also indicate the presence of interchain interactions in solutions of protonated PAni.[6,7]

Protonation of PAni has been followed by elemental analysis,[2,8] potentiometric titration[9,10] and various spectroscopic methods.[11,12] As most spectroscopic parameters do not yield a quantitative measure of the degree of protonation, the former two methods[8–10] are employed for measuring the degree of protonation of the polymer. It has been shown that the absorbance at *ca.* 800 nm, due to the polaronic band of PAni, does not change proportionally with the degree of protonation.[7] On the other hand, the degree of protonation of PAni is known to be dependent on the ionic strength of the protonating medium. This has been attributed to the Donnan potential[10,13] between the solid polymer phase and the aqueous phase owing to the presence of fixed positive charges on the protonated PAni. Protonation of PAni has also been followed using vibrational spectroscopy. A large shift of the mid-IR band for the N—H stretching mode is observed,[14] which has been ascribed to strong interchain hydrogen bonding between the positively charged amine groups and the imine nitrogens in protonated PAni. However, the shifted band appears only as a broad hump from *ca.* 1700 to 900 cm^{-1} and it is difficult to obtain quantitative information on hydrogen bonding in PAni from this band. Hence, it would be interesting to study the spectra of PAni in the far-IR region where the corresponding band due to the $NH^+ \cdots N$ hydrogen bond is expected to appear. Studies of hydrogen bonding would yield important information about the interchain interactions in PAni systems.

In the present work, a band at 130 cm^{-1}, tentatively assigned to the $NH^+ \cdots N$ hydrogen bond in the protonated emeraldine form of PAni,[2] is reported. The change in the absorbance of this band, along with the change in the near-IR band with the degree of protonation of the polymer, have also been studied. Though the effect of ionic strength on the degree of protonation of PAni is well known,[10,13] in the present paper the influence of the ionic strength on the vibrational as well as electronic (near-IR) absorbance spectra of PAni, at a particular degree of protonation, has been investigated. Based on the results it is suggested that ionic interactions and hydrogen bonding play vital roles in formation of the metallic islands[4] in PAni.

Experimental

PAni in the emeraldine form was prepared by the standard chemical method.[2] A fraction, soluble in dimethyl sulfoxide (DMSO) or *N*-methylpyrrolidone (NMP), was extracted from the undoped PAni powder and was used for all the following spectroscopic studies. For UV–VIS spectroscopic studies, a thin film of PAni was cast on the inside wall of a cuvette and equilibrated for at least 5 h with aqueous media of different ionic strengths (different concentrations of KCl) and of different pH (adjusted by the addition of aqueous HCl). The absorbance spectra of the polymer films in the region 280–875 nm were recorded using a Hitachi (U-3400) spectrophotometer, for each set of pH and ionic strength under *in situ* conditions, with the cuvette filled with the aqueous medium. The change in the absorbance of the film at 850 nm relative to that at pH 7 was measured at various pH values. For FTIR studies, a free-standing film of PAni cast from the solution was studied under *ex situ* conditions. The film was equilibrated with aqueous KCl solutions of different concentrations and pH. After at least 5 h of equilibration with each solution, the film was taken out, the excess solution was removed by pressing the film between filter papers and was then dried in vacuum at *ca.* 70 °C. PAni is known to be stable at this temperature.[15] The same film was used for each set of spectra relating to a particular ionic strength. The FTIR spectra of the PAni films were recorded using a Digilab FTS-60 spectrometer. Though in the FTIR experiment equilibrium conditions were not maintained, the Donnan effect is expected to be small at the high ionic strength of the medium (1 mol dm^{-3}).[13] Therefore, the change in the Donnan potential and, hence, in the degree of protonation of PAni, due to the increase in the concentration of the aqueous KCl solution absorbed in the polymer phase during the drying process, is assumed to be negligible.

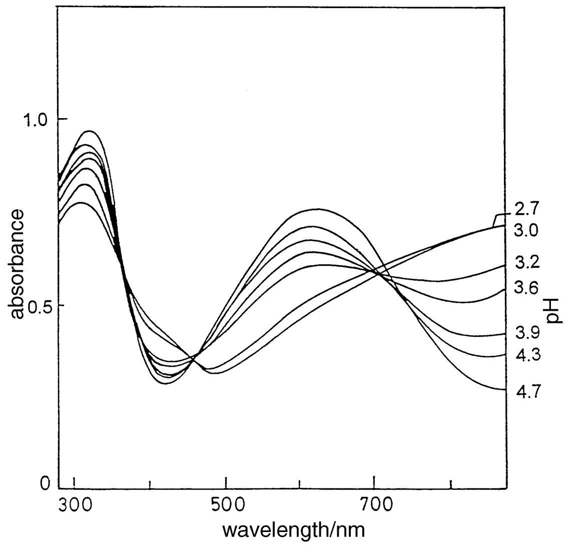

Fig. 1 UV–VIS spectra of PAni films in 1 mol dm^{-3} KCl solutions of different pH

Results

UV–VIS spectroscopy

UV–VIS spectra of PAni films equilibrated at different pH values are shown in Fig. 1. Upon protonation of PAni with decreasing pH, a band appears in the near-IR region due to the formation of positively charged polarons on the polymer chain.[16] The peak position of this band is above the limit up to which the spectra could be recorded for the present studies (Fig. 1). However, from the shape of the spectra it is evident that the absorbance due to the polaron band attains almost the highest value above 850 nm. Also, since 850 nm seems to be not too far from the peak position, it is reasonable to assume that absorbances at these two positions result from the same species and they would be proportional to each other. Therefore, the absorbance at 850 nm (A_p) is used as a measure of concentration of the charge carriers and, hence, of the amount of conducting phase in the system. The change in the absorbance at 850 nm upon protonation ($A_p - A_i$) was measured with respect to the absorbance at pH 7 (A_i). The relative change in the absorbance (χ) was calculated as

$$\chi = (A_p - A_i)/(A_f - A_i) \qquad (1)$$

where A_f is the maximum absorbance at 850 nm resulting from the protonation of the polymer. The degree of protonation of PAni at different pH values and ionic strengths can be obtained from the results of potentiometric titrations.[10] When χ is plotted against the degree of protonation of PAni (Fig. 2), it is observed that χ does not vary in a linear fashion. That is, the appearance of the polaron band is not directly related to the degree of protonation of the polymer. Further, the variation of χ is also dependent on the ionic strength of the medium. For the film equilibrated with lower ionic strengths, the polaron band appears even at low degrees of protonation and the change in χ is gradual, whereas at high ionic strength, the band appears only above a critical value of the degree of protonation and χ changes sharply thereafter.

Mid-IR spectroscopy

The mid-IR spectra of PAni, at the same degree of protonation of 0.27, but equilibrated with media of different ionic strengths, are shown in Fig. 3. The appearance of the broad hump in the baseline from *ca.* 1700 to 900 cm^{-1} has been attributed to the band for the N—H stretching mode, shifted owing to the hydrogen bonding in PAni.[14] It may be observed, particularly from the difference spectrum [Fig. 3(*c*)], that this band is stronger when the PAni film is equilibrated with aqueous media of lower ionic strength. The bandwidths of the other peaks in the spectrum are also increased (leading to the appearance of the sharp peaks in the difference spectra), possibly owing to the higher interchain hydrogen bonding interactions in the latter sample. It is also interesting to note

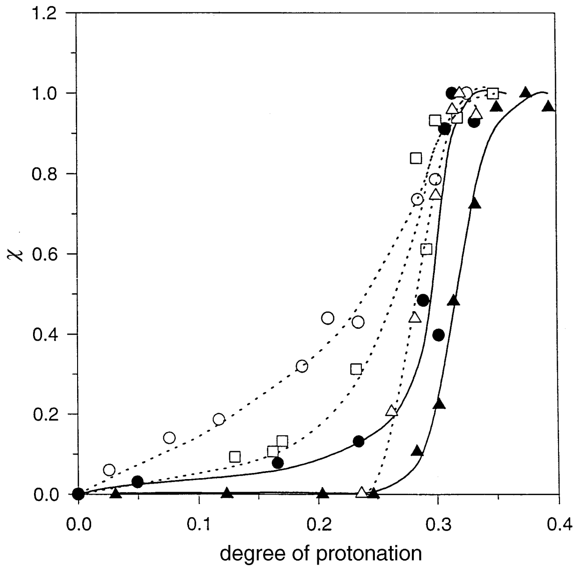

Fig. 2 Plot of the change in the relative absorbance (χ) at 850 nm from the UV–VIS spectra (···) and at 130 cm^{-1} from the far-IR spectra (—) *vs.* degree of protonation of PAni equilibrated with aqueous KCl solutions of different concentrations: ▲, △, 1 mol dm^{-3}; □ 0.1 mol dm^{-3}; ●, ○, 0.0 mol dm^{-3} KCl. The closed and open symbols correspond to the experimental points from the far-IR spectra and the UV–VIS spectra, respectively.

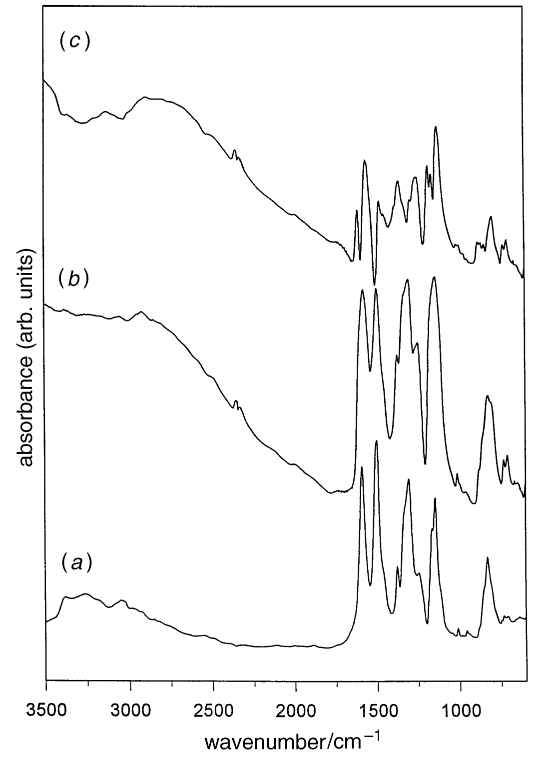

Fig. 3 Mid-IR spectra of PAni, with a degree of protonation of 0.27, equilibrated in aqueous KCl solutions at concentration of (*a*) 1 mol dm^{-3} (pH 4.2), (*b*) 0 mol dm^{-3} (pH 2.1); (*c*) spectrum obtained from subtraction of spectrum (a) from spectrum (b) after normalisation with respect to the peak at 830 cm^{-1} [(*c*)=(*b*)−1.14(*a*)]

that the broad absorbance above 1800 cm^{-1}, due to the tail of the electronic band of the free carriers associated with the conducting state of PAni,[14] is much stronger for the film equilibrated at lower ionic strength. This conforms with the above results from the UV–VIS spectra, which show that the near-IR band of the partially protonated PAni is stronger in low ionic strength media. Though the studies in the mid-IR region give some qualitative evidence of the hydrogen bonding in PAni and its dependence on the ionic strength of the protonating medium, the quality of information is not good enough for any quantitative analysis.

Far-IR spectroscopy

In the far-IR (450–75 cm^{-1}) spectra of PAni (Fig. 4), a peak at 410 cm^{-1}, which is present in the spectrum of unprotonated PAni, increases in intensity and a new broad band at *ca.* 130 cm^{-1} appears on protonation. The 410 cm^{-1} peak, which is also observed in Raman spectra of PAni,[17] has not been assigned. The 130 cm^{-1} band is assigned to hydrogen bonding between the charged amine groups and the imine nitrogens (*vide infra*). Owing to a better signal-to-noise ratio in the lower energy region, the 130 cm^{-1} peak was used to quantify the effect of protonation of PAni on its vibrational spectrum. The absorbance at 130 cm^{-1} was measured after correcting for the upward shift in the baseline of the spectra (Fig. 4) with protonation. The shift is probably caused by an increase in the reflectance of the polymer in the far-IR region upon formation of the conducting state with protonation, as reported earlier.[18] The relative change in the absorbance (χ) at 130 cm^{-1} is calculated using eqn. (1) and plotted against the degree of protonation of the polymer in Fig. 3. This shows that the change in absorbance of PAni in the far-IR region is also not directly proportional to its degree of protonation and is dependent on the ionic strength of the doping media. However, the dependence of χ on the ionic strength is found to be less for the 130 cm^{-1} band than for the 850 nm band. This may be due to the fact that in the far-IR experiment, the PAni film was dried before recording the spectra whereas the UV–VIS spectra were recorded *in situ*, keeping the film in equilibrium with the aqueous medium. Drying of the film in the former case changes the dielectric environment in the polymer phase, which may obscure the effect of the ionic strength on the far-IR absorbance. On drying, the absorbance at 850 nm was also found to decrease by a factor of three for the PAni film with a degree of protonation of 0.25.

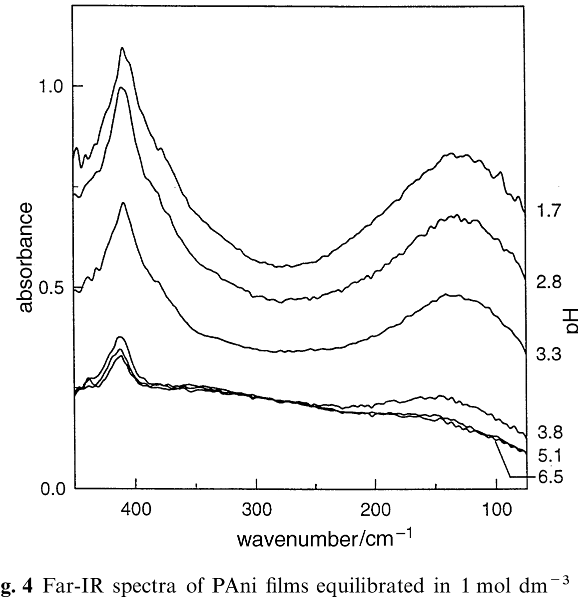

Fig. 4 Far-IR spectra of PAni films equilibrated in 1 mol dm^{-3} KCl solutions of different pH

Discussion

Upon protonation of PAni, localized charged sites are formed on the polymer backbone. As the degree of protonation is increased, the charged sites overlap to form the polaron band, leading to the appearance of the near-IR peak. The conductivity and the intensity of the EPR signal of the polymer change concomitantly with the near-IR band upon protonation.[19] Therefore, the absorbance of PAni in the near-IR region is related to the conducting state of the polymer. However, an ideal polaron lattice in PAni requires a degree of protonation of 0.5, whereas in the present study, as also observed earlier,[2,4] the conducting state in PAni appears at much lower degrees of protonation. This is due to the fact that the protonation of PAni is not homogeneous throughout the bulk—it occurs in clusters, leading to the formation of conducting domains in the polymer matrix, known as metallic islands.[4] The formation of such domains may occur due to phase segregation of the ionic species—the protonated portion of the polymer and the counter anions, in the low dielectric medium of the unprotonated polymer matrix. Such phase segregation is well known in ionomeric systems.[20] At low ionic strength, owing to the phase segregation, the local degree of protonation of the polymer in the ionic phase is high even at lower degrees of protonation of the bulk. This leads to electronic overlap of the charged sites on the polymer with the formation of the polaronic band and, hence, to an increase in the absorbance at 850 nm, whereas at high ionic strength, the charged sites on the polymer may be stabilised by the free ions present in the medium, preventing phase segregation at low degrees of protonation. Only at higher degrees of protonation do the charged sites come close together to interact forming the polaronic band. This seems to explain the observation that for high ionic strength of the doping medium, the 850 nm band appears only above a critical value of the degree of protonation (*ca.* 0.24).

The broad band from 1700 to 900 cm^{-1}, observed in the mid-IR spectrum of protonated PAni, has been interpreted as an N—H stretching band, shifted owing to strong interchain hydrogen bonding between protonated sites and the imine nitrogens ($NH^{+}\cdots N$).[14] Also, for imidazole, a shift in the N—H stretching frequency is observed, accompanied by the appearance of a band in the far-IR region at 142 cm^{-1}, which is assigned to the stretching mode of the $NH\cdots N$ hydrogen bond.[21] The broad far-IR band for PAni observed at *ca.* 130 cm^{-1} may therefore be tentatively assigned to the $NH^{+}\cdots N$ vibration. This is supported by the fact that the peak position remains unaffected on changing the acid for protonation of PAni from hydrochloric acid to sulfuric acid or acetic acid. However, no appreciable change in the peak position could be observed on exchanging the protons with deuterium ions by equilibrating PAni with HCl solution in D_2O. This may be due to fact that only a small change in the peak position is expected on deuterium exchange; the decrease in vibrational frequency due to the increase in the mass is partly compensated by the decrease in the zero-point energy due to a large anharmonicity in the potential-energy well of the hydrogen bond.[22] Also, since in the 130 cm^{-1} vibration mode the protonated imine group moves as a whole, the effect of the change in the mass, due to the isotope exchange, on the vibration frequency should be small. In the case of imidazole, a shift of only 9 cm^{-1} was observed.[21] In the present experiment, such a small change in the peak may be obscured by the broadness of the 130 cm^{-1} band.

In polymeric systems, interchain hydrogen bonding is often a cooperative phenomenon.[23] That is, the extent of hydrogen bonding depends non-linearly on the number of hydrogen bonding sites; the formation of a hydrogen bond occurs only when a critical number of consecutive hydrogen-bonding sites are present. This may explain the non-linear dependence of the absorbance of the 130 cm^{-1} band on the degree of protonation.

At low ionic strength, owing to phase segregation of the ionic groups, the local concentration of protonated nitrogens, which are also the hydrogen-bonding sites, is high in the ionic phase. Hence, in the ionic phase the critical number of consecutive hydrogen-bonding sites may be reached even at low degrees of protonation, leading to formation of the hydrogen bonds. At high ionic strength, owing to the decreased phase segregation, the extent of hydrogen bonding is decreased, lowering the intensity of the absorbance at 130 cm^{-1}. It should be noted however, that the present studies do not give conclusive evidence for assignment of the 130 cm^{-1} band to hydrogen bonding. Nevertheless, from the nature of its variation with the degree of protonation, the 130 cm^{-1} band seems to be associated with certain cooperative interactions in the system. Such interactions would also lead to phase segregation and the above discussion would hold good even if the band is due to any other cooperative intermolecular bonding in PAni.

UV–VIS spectroscopy therefore shows that the electronic properties of PAni are dependent on the ionic environment of the polymer chain. On the other hand, examination of the FTIR spectra indicate that the interchain interactions through the hydrogen bonding in PAni are also dependent on similar factors. Earlier studies[6,7] on PAni solutions in acidic solvents suggest that the electronic states pertaining to the near-IR transition extend in three dimensions and involve interchain electronic coupling. It is possible that the interchain electronic interaction is reinforced by the interchain hydrogen bonding. The observations in the present studies are in accord with the earlier observations that the optical spectra and other electronic properties of PAni are sensitive to the nature of the counter anion.[1,3] This dependence may be caused by the modification of the metallic islands (*i.e.* the segregated ionic clusters) by the surfactant anions, which determines the surface energy at the interphase boundaries. Therefore, examples showing the effect of intermolecular interactions on various properties of PAni are already available. However, the present investigations show the importance of ionic interactions and the involvement of interchain hydrogen bonding in PAni systems. The ionic strength not only determines the degree of protonation due to the Donnan effect, it also affects the distribution of ions and, hence, the electronic structure of protonated PAni.

In previous studies, the ionic strength of the medium for protonation of PAni has seldom been controlled. In a recent electrochemical study,[24] the mechanism of ion exchange during redox reaction on PAni-coated electrodes has been shown to be dependent on the ionic strength of the electrolyte solution. In industrial applications, since PAni may be used in conditions of different ionic strengths, knowledge of the dependence of the conducting state of the polymer on the ionic environment is of great importance. Apart from PAni, the formation of metallic clusters on doping is also observed in other conducting polymers such as polyacetylene.[25] It may be valuable to review earlier interpretations of results on doping of conducting polymers in the light of the present study.

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