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Zeta potential and doping in polyaniline dispersions

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Polyaniline (PAni) has been classified as an intractable polymer, particularly in its conducting form, the emeraldine salt (ES). Therefore one can consider the mixture of water and PAni as a suspension. The conducting form of PAni can be obtained by a doping process known as "acid doping", in which a strong acid turns PAni from its insulating form, the emeraldine base (EB), into the conducting form, the emeraldine salt. With the objective of establishing a correlation between the doping level and the zeta potential of polyaniline dispersions, polyaniline + HCl aqueous suspensions were prepared. Positive zeta potential values for the various suspensions of PAni showed that it acquired positive charges after the doping process. It was also observed an increase in zeta potential values as HCl concentration increased, which could be correlated to UV-visible spectra of PAni suspensions.

Key words: *polyaniline; electrophoretic mobility; zeta potential; doping*

1. Introduction

Polymers derived from organic compounds, with π-electron conjugation and high dopant concentration, are termed conducting organic polymers [1]. These polymers have been extensively studied by researchers due to their large variety of applications, such as rechargeable batteries [2], electrochromic devices [3] and luminescent materials [4] in optical devices. Among these polymers, polyaniline (PAni) is at an

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outstanding position, mainly due to the relatively simple experimental methods used in its synthesis [5]. This polymer may occur in different redox states, the main structures, as shown in Fig. 1, being leucoemeraldine (LEB), emeraldine (EB), and pernigraniline (PGB) [6]. All these basic forms are insulating ones. Doping is the reason for the high conductivity and other unique properties of conducting polymers [7]. The fundamental process of doping is a reaction of charge transfer between the organic polymer and a dopant: when charges are removed (or added) to a polymer chain through a chemical reaction, the geometric parameters, such as bond angles, lengths and hybridization, are modified, resulting in a drastic change in conductivity, the levels of doping and oxidation being the most important factors affecting the electric properties of polyaniline [8]. Different dopants produce polyanilines with different properties, suitable for specific applications [9, 10]. As an example, in the case of PAni films, one can find reported in the literature doping by chorona discharge [11]. In fact, one of the most common mechanisms of doping of polyaniline, according to the literature, is known as acid doping, where strong mineral acids change the insulating form EB into the saline conductive one ES [12], as displayed in Fig. 2.

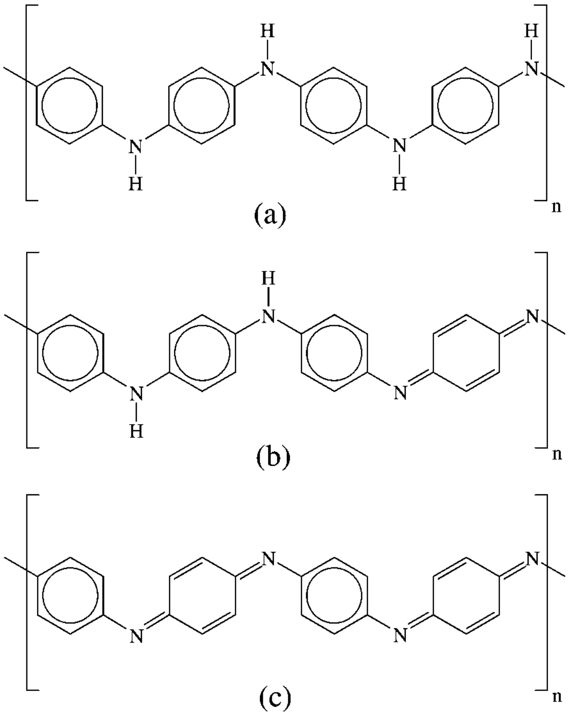

Fig. 1. Basic structures of polyaniline: a) leucoemeraldine base, b) emeraldine base, c) pernigraniline base

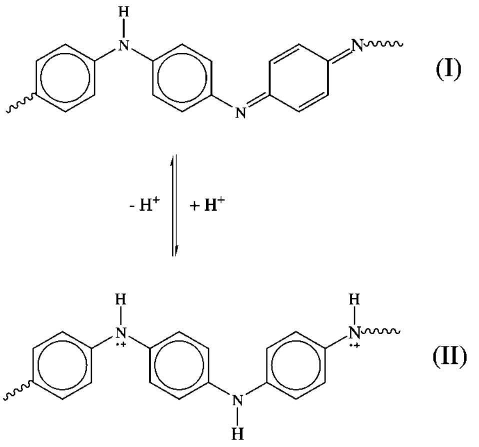

Fig. 2. Scheme representing doping of EB polyaniline for the obtention of emeraldine salt (ES)

Although acid doping occurs without any variation in the number of electrons of the polymeric chain, the protons introduce positive charges there. As a consequence, chemical interaction can be described as a two-stage process [13]:

$$\mathrm{EB} + \mathrm{HA} \rightarrow \mathrm{EB(H{-}A)_{adsorbed}} \tag{1}$$

and

$$\mathrm{EB(H{-}A)_{adsorbed}} \rightarrow \mathrm{EB{-}H^{+}} + \mathrm{A^{-}} \tag{2}$$

where Eq. (1) represents the interaction of the imine polymer group with the acceptor molecule H–A, through hydrogen bonding, and Eq. (2) is the charge separation process in these adsorption complexes. Obviously the acid molecules may react with EB in a similar way and, in a strongly acid medium, the last reaction is equivalent to the acid doping and to the conversion of EB into ES. In this way, we can describe the acid doping of EB as an interaction donnor-acceptor followed by charge separation (charge transfer) in the formed complex. The hydrogen bond given by an acceptor molecule is incorporated to the donnor molecule in the second stage of the transformation.

Polyaniline has frequently been classified as an intractable polymer, particularly in its conductive form, the emeraldine salt (ES). It is feasible, as a consequence, to consider the mixture of polyaniline and water as a colloidal suspension [14], which, depending on the application, may become a problem for the processing of this polymer. As a consequence, the study of particle interactions in these colloids, together with new methods of preparation represents an important step for obtaining dispersions which could be used in an increasingly wider range of technological applications [15]. Regarding particle morphology, Stejskal et al. [16, 17] have analyzed the influence of experimental conditions on the particle shape and size of polyaniline dispersions stabilized by different hydrophilic polymers.

In any colloidal system, several aspects of its behaviour (e.g. rheology [18] and stability [19, 20]) are highly governed by particle–particle particle–solvent interactions. Regarding purely electrostatic interactions, these interactions have been described by the so-called DLVO theory [21], one of its main parameters being the ζ potential, which is defined as the electrical potential at the particle double layer shear plane [22]. This potential, in its turn, is governed by surface particle charges: the higher the density of positive charges, the more positive this potential will be (the opposite being true for negative charges) [23]. The aim of this work is to correlate the level of doping of polyaniline particles (in aqueous suspensions) with ζ potential values of these very particles and relate these data to measurements of electromagnetic absorption in the UV-visible region.

2. Experimental

The polyaniline used in this work was synthesized at the Instituto de Física de São Carlos as described in the literature [24]. The suspensions of PAni in dilute HCl were obtained by the dispersion of 0.05 g of PAni in 50 cm^3 of aqueous solution of HCl. Bidistilled water was used in all experiments. The suspensions were prepared with HCl solutions with the following concentrations: 0.2 mmol/dm^3, 1 mmol/dm^3, 2 mmol/dm^3, 4 mmol/dm^3, 6 mmol/dm^3, and 8 mmol/dm^3. The dispersions were sonicated for 60 s and left at a room temperature for 24 h, since it has been found that sonication of PAni-containing particles would result in their desintegration, generating unstable nanoparticles, which undergo fractal aggregation [25]. Afterwards, ζ potential and electromagnetic absorption measurements were carried out.

2.1. Electrophoretic mobility and ζ potential measurements

The electrophoretic mobility measurements μ_E were carried out using a Zeta-Meter System 3.0+ (Zeta-Meter Inc., USA). The ζ potentials of the polyaniline suspensions were calculated from μ_E by employing the Smoluchowski relationship, assuming that $\kappa a \ll 1$, where κ is the Debye–Hückel parameter and a is the radius of the particles [26]:

(3)

where ε_0 is the permittivity of vacuum, ε is the relative electric permittivity of water, and η is the viscosity of the disperser phase.

2.2. UV-visible spectroscopy

UV-visible absorption spectra of the suspensions were obtained using a Cary spectrophotometer, model 1E, at room temperature.

3. Results and discussion

Figure 3 displays the values of ζ potential for the polyaniline particles as a function of pH of the disperser phase. One can observe that all potential values are positive, indicating that polyaniline acquired positive charges as a consequence of doping, as discussed before. One can also observe that, as pH decreases, ζ potential increases. It is due to the fact that as more H^+ ions are present in the disperser phase, more polyaniline chains will be doped, implying an increase in the charges on these chains (and, consequently, on the particles surface). As a consequence they move faster than the less doped particles when submitted to the same potential gradient. Butterworth et al. [27] have found the same results with polyaniline synthesized *in situ* with ultrafine silica. In this case, the effect could not be solely related to PAni doping, since polymerization conditions resulted in obtaining particles with a "raspberry" morphology, resultant of bridging flocculation of silica through polyaniline-oxide interaction: as a consequence, an increase in ζ potential with the acid concentration could also be the outcome of neutralization of negative sites which may exist on the silica surface [28].

Fig. 3. ζ potential as a function of pH for polyaniline dispersions

If, as seen in the zeta potential measurements, the change in ζ potential for pure polyaniline were due to doping, these changes should be related to changes in the UV-visible absorption spectra of these dispersions. This relation is depicted in Fig. 4, in which UV-visible absorption spectra are plotted as a function of pH for polyaniline dispersions. One can observe in the referred figure that the spectra gradually change from the emeraldine base (pH = 5.6), and, in the more acid conditions (pH = 2.2), the changes in the structure of polyaniline are much more evident in the spectrum, which is characteristic of the emeraldine salt, the doped form of polyaniline [29, 30]: the bands which arise at 435 nm and 720 nm are attributed to the electronic excitation of benzenoid and quinoid rings; increase in protonation of imine groups firstly results in the occurrence of polarons and further protonation results in an increase in the range of polaron-related conjugation, resulting in a decrease in polaron band energy (shift from 720 nm to 860 nm, blue to dark green). The band at 338 nm appears due to the transition of the conjugated aromatic ring [31], more specifically to a π-π^* transition.

Fig. 4. UV-visible absorption spectra of polyaniline dispersions

According Banerjee et al. [32], polyaniline dispersions should not present more changes in UV-visible spectra for pH below 4, but they observed these changes in PAni–PMVE dispersions; they attributed them to different particle sizes or different macromolecular chain packing: if the same is true for our experiments, it could be the case that, in the present work, pH has influenced macromolecular packing and/or particle size of redispersed PAni; however, in order to inequivocally affirm it for our experiments, light scattering measurements would be necessary.

4. Conclusion

Zeta potential measurements may be used to characterize doping in polyaniline suspensions. The values of zeta potential increase with increasing doping degree of these polymers, as can be confirmed by UV-visible absorption spectroscopy.

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