



Study of Polyaniline Oxidation Kinetics and Conformational Relaxation in Aqueous Acidic Solutions



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ABSTRACT

The oxidation kinetics of the polyaniline was investigated in aqueous solutions by potential steps for different values of the experimental variables. The chronoamperometric responses present a maximum, as described by the Electrochemically Stimulated Conformational Relaxation (ESCR) model. The empirical reaction kinetics $R = k[\text{ClO}_4^-]^\alpha [\text{pAn}^+(\text{qH}^+)]^\beta [\text{H}^+]^{-\gamma}$ was corroborated from the experimental results. The kinetic magnitudes: rate coefficients, reaction orders or activation energy were obtained. The value of each of those kinetic magnitudes change as a function of the initial reduced and packed state used for the subsequent oxidation: they include quantitative structural information about the structural conformational packing state of the chains in the initial state of the material. The fractional reaction order indicates, as expected, the existence of a complex mechanism for the oxidation reaction.

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1. Introduction

Redox reaction of conducting polymers involve a series of simultaneous events such as: electronic charge transfer, exchange of ions for charge balance, egress-ingress of solvent molecules for osmotic balance, and conformational movement of the polymer chains, taking place in a dense polymeric gel [1,2]. Some of the most important promised applications of these polymers as artificial muscles are directly related to these phenomena occurring during reverse electrochemical oxidation and reduction [3]. When the polymer immersed in a solvent containing suitable electrolyte is subjected to anodic (oxidation reaction), or cathodic (reduction), overpotentials, electrons are removed from, or injected to, the polymer backbone and charge compensating counter ions and solvent molecules diffuse into, or outside, polymeric matrix. Conformational movements of chains take place opening, or closing, the involved free volume. Any theoretical description of this process should include the kinetics of electrochemical reaction and conformational movements of the polymeric chains [4–12].

Polypyrrole oxidation kinetics in aqueous and acetonitrile solutions have been studied by Otero et al. [9,10]. In both solutions, the rate coefficients (k) and activation energies (E_a) change as a function of the initial packed state of the polymer: lower values of k and rising values of E_a are obtained from rising reduced and packed

initial states obtained by reduction at more cathodic potentials. The activation energy includes two components the constant chemical activation energy and the energy of the packed conformations. Rising activation energies were attributed to more packed conformations of the initial states. It was shown that the attained k from aqueous solutions, ranging from 1.05 to $0.77 (\text{Imol}^{-1})^{1-(\alpha+\beta)} \text{s}^{-1}$ are smaller than those obtained from acetonitrile ranging from 3.63 to $0.33 (\text{Imol}^{-1})^{1-(\alpha+\beta)} \text{s}^{-1}$. The rate of decrease on the rate coefficient by increasing the reductive prepolarization time or potential attained in aqueous solution is less than that obtained in acetonitrile indicating the polymer more easily is packed in acetonitrile by electrochemical reduction [9,10]. Also it was shown that the activation energy for the oxidation of polypyrrole after reduction includes two components: the constant chemical activation energy and the conformational activation energy [9]. The chemical and conformational activation energies in aqueous solution were 29 kJ mol^{-1} and $0\text{--}10 \text{ kJ mol}^{-1}$ (depending on initial packing state) respectively. However in acetonitrile, these parameters were around the 12 kJ mol^{-1} and $0\text{--}36 \text{ kJ mol}^{-1}$ [9,10]. These great differences were attributed to the presence of different solvents and different molecular interaction (polymer-solvent, ion-solvent) inside the polymer [10,13,14].

Electrogenerated films of polyaniline (PA) were also studied by chronoamperometry in acetonitrile solution by Otero et al. [4,15] to check for the presence of compaction, relaxation and diffusion processes such as those described by the electrochemically stimulated conformational relaxation (ESCR) model in polypyrrole. Acetonitrile was selected to avoid both proton discharge during cathodic compaction of the film at high cathodic potentials and

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anion exchange during redox processes. They showed that the redox process in aprotic solvent can be described by ESCR model. This model includes several constants which are specific for every studied polymer. Those constants are:

- The charge required to close and compact one mol of polymeric segments (z_c) by cathodic polarization;
- The charge required to relax and open one mol of compacted polymeric segments (z_r) by anodic polarization;
- The starting oxidation potential for a noncompact film (E_{\circ});
- The cathodic potential where the compaction starts (closing potential) (E_s);
- The conformational energy consumed per mole of polymeric segments to be opened in the absence of any electric field (ΔH^*) and
- a diffusion constant (b).

However acetonitrile is a solvent with the high ion-solvent interaction and very low solvent-polymer interaction. The presence of strong solvent-polymer or solvent-ion interactions allow the incoming of the anions into the polymeric structure to stabilize the positive charges formed and to help for the matrix expansion [13,14]. Conversely it was shown that the water with high dipole moment and low polarizability can penetrate in large amount into the polymeric structure to expand to a greater extent [14]. The role played by the counterions diffusion through the swelling/shrinking films and the influence of the structural state on the magnitude of the diffusion coefficient has been previously treated [16,17].

The objectives of this ongoing study are to develop experimental chronoamperograms from PAN in aqueous acidic solutions which involve the chemical and conformation kinetics of oxidation process. In this work, aqueous acidic solution was selected as electrolyte medium because experimental observations supported this fact that artificial muscles work preferentially in solvents having high interactions with the polymer, such as water [14]. Therefore, studying the chemical and conformational kinetics of oxidation of polyaniline in aqueous solution has some considerable aspects which should be noted. For this purpose, polyaniline was electro synthesized at constant potential and then investigated in perchloric acid solutions by chronoamperometric method.

2. Experimental

2.1. Chemicals and electrochemical equipments

Aniline (Merck) was distilled under reduced pressure to obtain colorless purified aniline and stored at -4°C . Perchloric acid and NaClO_4 (Merck) were used as supporting electrolyte in electrochemical experiments. All solutions were prepared using doubly distilled water. All the electrochemical experiments were performed with a potentiostat-galvanostat Autolab Instrument model PG-302 N. Two stainless steel 316 electrodes having 2.8 cm^2 and 3.0 cm^2 area were used as working and counter-electrodes, respectively. They were mirror-polished using a commercial polishing paste before use. Then the electrodes were cleaned and rinsed severely first with distilled water and then with acetone for several times. The reference electrode was a Metrohm Ag/AgCl (sat.KCl) electrode.

2.2. Polyaniline electrosynthesis

Polyaniline films were potentiostatically grown on the working electrode from 0.1 M aniline and 1.0 M HClO_4 aqueous solutions at 1.0 V (vs. Ag/AgCl) until 250 mC final consumed polymerization charge was achieved. The coated polyaniline electrodes were rinsed

with distilled water thoroughly before experiments. The electrochemical experiments were carried out at room temperature. When the effect of temperature was studied a water bath/thermostat ($\pm 0.5^{\circ}\text{C}$) was used to set the temperature at predefined value.

2.3. Experimental methodologies

After the electrochemical synthesis of a film, the coated electrode was transferred to the control solution. The polyaniline oxidation-reduction processes were studied in HClO_4 aqueous solutions by consecutive potential steps. The polymer was reduced by polarization at a different cathodic potential (E_c , ranging from -100 to -350 mV) for 60 s every time. Then the potential was stepped to an anodic potential (E , ranging from 300 to 500 mV) for a time long enough to allow the polyaniline oxidation. Most of the chronoamperometric responses show a maximum indicating that the oxidation begins under nucleation/conformational relaxation kinetic control [4–6,9–12,15]. Under those conditions, by changing one of the variables every time the time at the chronoamperometric maximum is expected to be influenced by: the cathodic polarization potential [9,10], the polarization time [10], the oxidation potential [9–12], the temperature [9] of the electrolyte, and the electrolyte concentration [9–12]. The current at the maximum defines the initial oxidation rate of the oxidation kinetics [9–12]. In order to check those dependencies, the experimental results were obtained by changing the above-mentioned variables one-by-one.

It is well established in literature that polyaniline can exist in three different oxidation states (Scheme 1) depending on the relative number of benzenoid and quinoid structures in the polymer [18–21]. These states are known as completely reduced leucoemeraldine base (L), intermediate emeraldine (E) and the fully oxidized pernigraniline (P) states. The situation can, in fact, be more complex because all these three species can get protonated to some extent, as a result of which the polymer can exist in its base form or as protonated salt for each of these oxidation states, particularly in highly acidic solutions (Scheme 1). In the case of polyaniline in HClO_4 aqueous solution starting from a reduced film (protonated Leucoemeraldine), the polymer oxidation reaction involves two steps [18–21].

3. Results and discussion

Fig. 1 shows the stationary voltammetric responses (after three consecutive potential sweeps) in 1.5 M HClO_4 aqueous solution at 50 mVs^{-1} . This response indicates that the main redox processes take place in the polyaniline film in the potential range between -100 and 400 mV . Deeper reduced, or oxidized states can be achieved at more cathodic, or more anodic, respectively, potentials. As stated by the ESCR model, and can be corroborated from the voltammograms and the concomitant coulometric results presented by Fig. 1 the reduction goes on beyond the reduction maxima (beyond the closing potential) at a slower reduction rate because the ions must migrate towards the solution moving apart the PANI chains. It is observable that the charge evolution (the PANI reduction) goes on up to the cathodic potential limit (Scheme 2).

Fig. 2 shows the anodic chronoamperometric responses (the oxidation kinetics) of the polyaniline film in 1.5 M HClO_4 aqueous solution, after reduction by prepolarization at different cathodic potentials (-100 , -150 , -200 , -250 , -300 and -350 mV) kept for 60 s every time, and then oxidized by potential step to the same anodic potential of 400 mV every time. As expected from the relaxation model, after deeper reduction and conformational compaction at more negative potential slower film oxidation reactions result. The oxidation chronoamperometric responses present a maximum that shifts to lower currents and longer oxidation

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