J. Chem. Research (S), 1999, 622–623†

The Autocatalytic Oxidation of Aniline by Persulfate and Permanganate as a Means for the Deposition of a Thin Polyaniline Film†

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The autocatalytic oxidation of aniline in an acidic solution with persulfate and permanganate, followed by the use of UV–Vis spectroscopy, leads to the deposition of a thin layer of the reaction product polyaniline onto glass and platinum.

Polyaniline and its derivatives are increasingly being used in various fields of science and technology. Polyaniline can be obtained either by electrochemical or by chemical oxidation of aniline. In the latter case, various oxidants have been reported to be suitable in obtaining polyaniline, *e.g.* ferrous ions,[1] dichromate,[2] persulfate[3] and hydrogen peroxide.[4] Both bulk polymer and a polymer film, deposited onto various conducting or non-conducting surfaces, can be obtained by chemical oxidative polymerisation of aniline. In this paper, we report the chemical polymerisation of aniline by persulfate and permanganate.

The experiments on the reaction kinetics were performed in a 2 mm path length quartz cuvette with the use of a dual beam Specord UV-Vis spectrophotometer. All solutions used contained 0.5 M H_2SO_4. The reaction kinetics were followed at a constant wavelength of 715 nm. Electrochemical experiments were done in a standard three-electrode cell with the use of PI-50 model potentiostat.

Results and discussion

After the addition of ammonium persulfate (APS) to an acidic solution of aniline, no remarkable changes are observed in the few first minutes. After that, the solution turns blue, indicating the oxidation of aniline, leading to coloured products. Fig. 1 (solid lines) shows the kinetics of the colouration of a reaction solution, observed upon addition of different concentrations of APS. The incubation period, where almost no increase of absorbance is observed, varies from *ca.* 25 to 10 min by increasing the APS concentration from 0.5 to 2.5 mM. After that, a rapid increase of absorbance is observed. The growth rate of absorbance also increases with increasing concentration of APS. In some experiments, the concentration of aniline was also varied within the range of 10 to 100 mM, indicating an increase of the reaction rate with increasing concentration of oxidant APS (not shown). The results obtained indicate an autocatalytic reaction of aniline with APS. As a result, the oligomers (mostly di- and trimers) of aniline, absorbing in the red region of the visible spectrum, are formed, as shown elsewhere, especially for the electrochemical oxidation of aniline.[5] Once formed, the oligomers catalyze the oxidation of aniline by APS. Thus, the autoacceleration is observed.

After a definite time, the absorbance of the reaction mixture reaches its maximum value, and then decreases to some extent. At this point, insoluble reaction products, presumably polyaniline, are formed from the oligomers. These products precipitate in the form of dark blue coloured solids. However, some polyaniline deposits onto the walls of the glass cuvette used, forming a thin visible greenish blue film. This chemically deposited film shows typical UV–VIS spectra (not shown), quite similar to those obtained by electropolymerisation on transparent electrodes.[6] By repeating the oxidation of aniline with APS in the same cuvette, which now contains a thin layer of deposited polyaniline, a much faster growth of absorbance, and thus much faster oxidation of aniline, is observed (dashed traces in Fig. 1). This indicates that the chemical interaction of aniline with APS is highly accelerated not only by the soluble products of reaction (*i.e.* oligomers of aniline), but also by the heterogeneous film of polyaniline. Probably, autoacceleration proceeds in this case at the polyaniline/solution interface more rapidly than in the bulk of solution. It was observed that a much thicker layer of polyaniline is deposited on the inner walls of the cuvette upon repeating the chemical reaction for the second time.

Another oxidant tested, potassium permanganate, oxidises aniline much faster, as evidenced by spectroscopic kinetics. As seen from Fig. 2, the reaction also proceeds in an autocatalytic manner, although the incubation period does not exceed *ca.* 1 min, even at a low concentration of both reactants. At any constant concentration of aniline, the reaction proceeds faster with a higher content of permanganate, and an increase of aniline concentration also

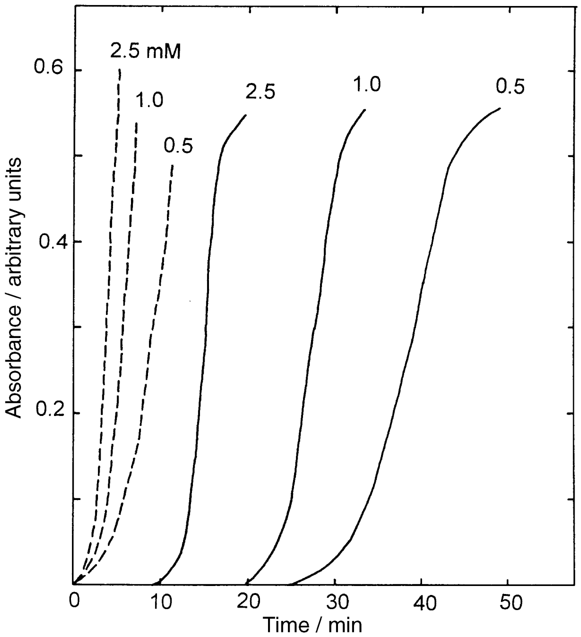

Fig. 1 Solid traces: growth of absorbance at 715 nm, obtained for the reaction mixture containing 0.5 M H_2SO_4, 25 mM of aniline, and different concentrations of APS (in mM, as indicated); dashed traces: same as above, but obtained from a second reaction in the same cuvette

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

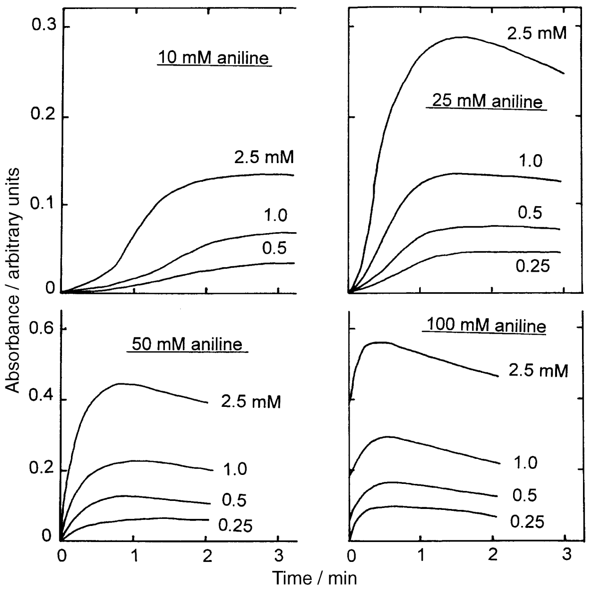

Fig. 2 Kinetic dependencies for the reaction of aniline with potassium permanganate, obtained for different concentrations of the reactants (in mM, as indicated)

causes an increase of the reaction rate (Fig. 2). As for APS, the deposition of a thin layer of polyaniline was observed on the inner walls of the reaction vessel. Also, autoacceleration proceeds faster in a reaction vessel containing a thin layer of polyaniline on the inner walls, *i.e.* by repeating the same experiment for the second time in the same vessel.

The deposition of a polyaniline layer was also shown to proceed on a platinum wire immersed into reaction solution. As a result, a thin layer of polyaniline is deposited on platinum, which shows its usual electrochemical redox activity when used as an electrode (Fig. 3). An usual anodic peak at *ca.* 0.22 V, as well as its cathodic counterpart at 0.05–0.10 V, are well seen. Thicker films of polyaniline, which correspond to higher anodic peaks, were obtained by the use of higher concentrations of APS (Fig. 3). Polyaniline-modified electrodes were shown to be electrocatalytically active in the electrochemical redox reaction of the hydroquinone/benzoquinone redox couple, decreasing the peak separation from *ca.* 0.26 V to 0.03–0.04 V. In this respect, the modified electrodes obtained are closely similar to those prepared by the electropolymerisation procedure.[7]

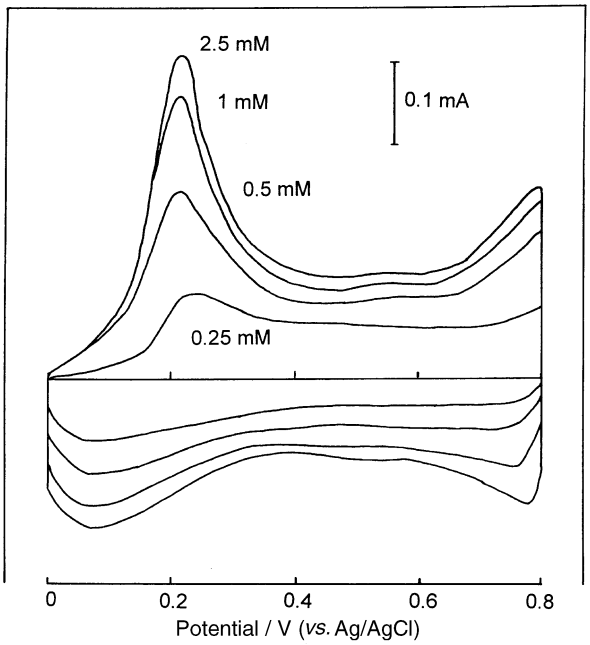

Fig. 3 Cyclic voltammograms obtained in 0.5 M H_2SO_4 at a potential scan rate of 50 mV s^{-1} with a platinum wire electrode that had been covered with polyaniline layer by its immersion for 1 h into a reaction solution containing 100 mM of aniline and different concentrations of APS (as indicated, in mM)

In conclusion, both oxidants used, APS and permanganate, are able to oxidise aniline in an autocatalytic manner, yielding thin films of polyaniline that are deposited both onto the walls of a reaction vessel, and onto the surface of platinum immersed into the reaction solution.

Received, 24th May 1999; Accepted, 5th July 1999
Paper E/9/04128A

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