Photogalvanic Cell: Iron(II)-Poly(N-acrylamidomethylthionine) System

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Thionine has been condensed with poly(N-methylolacrylamide) to give a polymer-dye complex and the spectral and photogalvanic properties of the complex have been studied. Depending on the polymer-dye ratio, a bathochromic shift is observed as compared to the spectrum of free thionine. Photogalvanic potential is found to depend strongly on the polymer-dye ratio.

The possibility of utilizing iron-thionine photoredox reaction in the construction of a photogalvanic cell for converting solar energy into electrical energy was first studied by Rabinowitch in 1940. Several independent groups studied the kinetics and mechanism of this reaction.

In Rabinowitch’s cell, two identical platinum electrodes were used with one illuminated and the other kept in dark. Recently devised totally illuminated thin layer (TI-TL) cell employs a transparent and selective anode and a platinum cathode. The selectivity of the SnO₂ electrode, which responds more readily to the dye redox couple than to the Fe²⁺/Fe³⁺ couple, removes the requirement of separating the illuminated and dark cell compartments. One of the serious problems with the iron (II)-thionine system or with any photogalvanic cell is the back thermal reaction which reduces the efficiency of the cell. In order to reduce the back reaction, in the present work, thionine has been condensed with poly(N-methylolacrylamide) and the photogalvanic effect of iron (II)-poly(N-acrylamidomethylthionine) system has been investigated. The effects of P/D ratio (number of mol of monomeric units/number of mol of dye) and aqueous-organic solvents on the absorption spectra of poly(N-acrylamidomethylthionine) and on the photogalvanic effect of iron(II)-poly(N-acrylamidomethylthionine) system are also discussed.

Materials and Methods

Apparatus — Totally illuminated thin layer cell consisting of the anode (1 sq cm) of corning EC glass coated with thin film of SnO₂ and the cathode (1 sq cm) of platinum plate was used. The distance between the electrodes was 4 mm. In all the experiments polymeric dye solution (10 ml) with absorbance of 0.86 was taken in the cell. The solution was deaerated as well as stirred at a constant rate by bubbling oxygen-free nitrogen through it. For irradiation of the solution, a parallel beam from a 500 W projector lamp filtered through a cell containing water was used.

Open circuit photopotential was measured using an ‘Aplab’ microvoltmeter and the current measurements were made using Metrimpex Universal polarograph, type OH-105. The absorption spectra were measured with a Carl-Zeiss UV-Vis spectrophotometer.

Reagents — Thionine, obtained as thionine chloride (Riedel, Germany) was used after purifying by the method of Clark and Eckert. Thionine chloride is converted into the free base by adding 10% sodium hydroxide to an aq. solution of thionine chloride. The free base was then collected with a gravity filter and dissolved in hot 2-propanol. The hot solution was treated with activated charcoal, filtered while hot and left to stand overnight under N₂ at room temperature. The crystals obtained were separated by decantation and introduced into a solution of hydrochloric acid (1.1 M) and stirred for 1 hr. The resulting crystals were recrystallised from 2-propanol-water (50% v/v), washed with cold 2-propanol and dried in vacuo.

N-Methylolacrylamide was prepared following the procedure of Feuer and Hart. A mixture containing acrylamide (35.5 g), paraformaldehyde (15 g), methylene chloride (300 ml) and colloidal sodium persulphate in xylene (2 ml) was refluxed for 30 min. The hot solution was filtered, cooled in ice-bath, crystalline solid collected and recrystallised from methylene chloride.

Poly(N-methylolacrylamide) was obtained by the polymerization of N-methylolacrylamide in aqueous solution. Distilled water (250 parts) at pH 5.7 was heated to 50°C, when nitrogen was passed through. N-Methylolacrylamide, isopropanol and ammonium persulphate in the ratio (25 : 1.5 : 0.5) were added to this solution and the temperature of the mixture was maintained at 60°C for 2 hr. Poly(N-methylolacrylamide) which precipitated on adding methyl alcohol as non-solvent was purified by repeated precipitation.

Poly(N-acrylamidomethylthionine) was prepared by condensing poly(N-methylolacrylamide) with thionine following the procedure of Kamogawa et al.
Purified thionine and poly(N-methylolacrylamide) in various ratios in water were heated at 90° for 5 hr. The condensed polymer(I) was precipitated using large amount of methanol and purified from the uncondensed thionine by dialysis.

Results and Discussion

Absorption spectra of poly(N-acrylamidomethylthionine)—The absorption spectrum of dil. aqueous solution of thionine exhibits a strong and sharp peak at 600 nm (α-band) and a weak shoulder at 568 nm (β-band). The α- and β-bands have been assigned to monomeric thionine and dimeric and higher aggregates of thionine respectively. When thionine is condensed with poly(N-methylolacrylamide) with $P/D = 33$ and 96 a small bathochromic shift is observed (Fig. 1). The α-band at 614 nm instead of 600 nm and β-band at 580 nm instead of at 568 nm). With the decrease in $P/D$ ratio, the intensity of α-band is decreased and that of β-band is increased. When $P/D = 16$ the intensity of α- and β-bands are nearly equal and at $P/D = 1$, the α-band becomes the shoulder and the β-band shows a clear maximum. This effect is due to the formation of the dye-aggregates in the macromolecule due to hydrophobic interaction.

Addition of organic solvents to the aqueous solution of poly-N-acrylamidomethylthionine decreases the extent of aggregation. The effect of 40% (v/v) acetonitrile-water and 40% (v/v) ethanol-water mixtures on the absorption spectrum of the polymer-dye with $P/D = 16$ is shown in Fig. 2. As the hydrogen bonding ability of the solvent is decreased, the extent of aggregation due to hydrophobic interaction is minimised. The percentage of organic solvents could not be increased above 40% due to the insolubility of the polymer.

Photogalvanic effect—Acidic solution of poly(N-acrylamidomethylthionine) containing ferrous ion shows galvanic photopotential on illumination with visible light. In the TI-TL cell with SnO$_2$ semiconductor and platinum electrodes, iron(II)-poly-(N-acrylamidomethylthionine) shows a negative photopotential similar to that of iron (II)-thionine system. At the SnO$_2$ electrode the dye/redox couple is electrochemically more reactive than the Fe$^{3+}$/Fe$^{2+}$ couple. Hence SnO$_2$ electrode acts as anode and the platinum electrode, where Fe$^{3+}$/Fe$^{2+}$ redox reaction takes place acts as the cathode.

The electrode reaction at SnO$_2$ anode is

$$\text{TH}_3 \rightarrow \text{TH}^+ + 2\text{H}^+ + 2\text{e}^-$$

and the electrode reaction at the cathode is

$$\text{Fe}^{2+} + \text{e}^- \rightarrow \text{Fe}^{3+}$$

The effect of $P/D$ ratio of poly(N-acrylamidomethylthionine) on the open circuit photopotential ($V_{oc}$) and short current circuit ($I_{sc}$) is shown in Fig. 3. The $V_{oc}$ and $I_{sc}$ first increase as the $P/D$ ratio increases and reach a maximum around $P/D = 33$ and then begin to decrease. In poly(N-acrylamidomethylthionine) with $P/D = 1$, the dye molecules are attached with all the monomeric units and aggregates are formed due to hydrophobic interaction with all the thionine molecules present in the form of aggregates as evidenced from the absorption spectrum. The aggregates of thionine are not photoelectroactive and also function as inner filters to reduce absorption by the monomer and show no
The power-output of iron(II)-poly(N-acrylamidomethylthionine) system is nearly 1/4th that of ironthionine system under identical conditions. Since thionine is attached as a side group in the polymer chain, the diffusion rate may be less than that of pure thionine, which is the rate-determining step for the electrode reaction. This defect can be overcome if the polymer is made into a thin film and then used.

The polymers with low $P/D$ ratio show less photopotential due to aggregate formation. When $P/D$ ratio is increased to eliminate aggregation, the internal resistivity of the polymer is increased, thus decreasing the galvanic effect. If a copolymer of N-acrylamidomethylthionine with some other monomer, whose flexibility is less, is prepared the aggregation may be prevented and at the same time it may have low internal resistivity. So, it may give higher power output than that of iron(II)-thionine system.

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**References**