ROLE OF AZINE DYE AS PHOTOSENSITIZER IN SOLAR CELL : GLUCOSE-SAFRANINE SYSTEM

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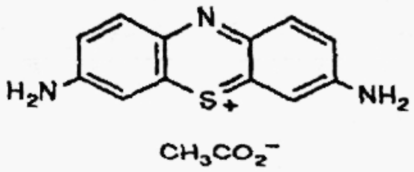
Abstract : Photogalvanic effect was studied in photogalvanic cell containing safranine and glucose as photosensitizer and reductant, respectively. The photopotential and photocurrent generated by the system was 373 mV and 35 μ A respectively. The effects of different parameters on electrical output of the cell were observed and a mechanism has been proposed for the generation of photocurrent in photogalvanic cell.

Introduction

Phenothiazines are important enough for their medicinal uses and bioanalytic applications. Phenothiazine dyes are successful photosensitizers also in photogalvanic cells for solar energy conversion and storage and among these, thionine 1 was used for the first time by Rabinowitch (1) to observe the photogalvanic effect in thionine-iron in a systematic manner. Later on, this work was followed by many workers (2-8) all over the world. Various problems encountered in the development of this field have been discussed by Hoffman and Lichtin (9). Theoretical conversion efficiency of photogalvanic cell is about 18 % but the observed conversion efficiencies are quite low due to lower stability of dyes, back-electron transfer, aggregation of dye molecules around electrode, etc.

A detailed literature survey reveals that different photosensitizers have been used in photogalvanic cells, e.g. riboflavin 2 (8), brilliant cresyl blue 3 (10), methylene blue 4 (11), toluidine blue 5 (12,13) and Azur C 6 (14) but no attention has been paid to use of azine dye as photosensitizer in photogalvanic cells for solar energy conversion, and therefore, the present work was undertaken by selecting Glucose-Safranine 7 system for this purpose



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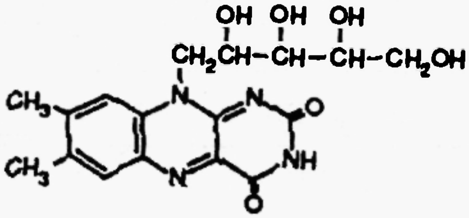

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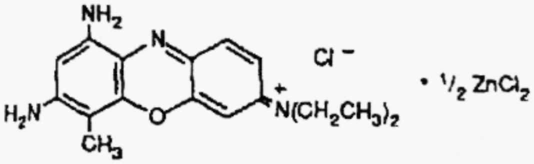

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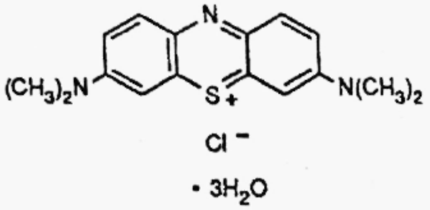

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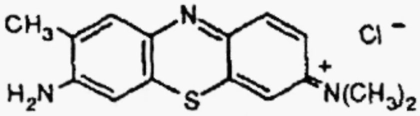

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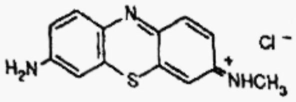

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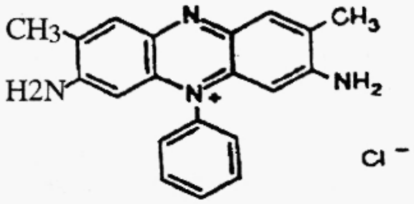

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Experimental

Safranine (Loba), Glucose (Qualigens) and Sodium hydroxide (s.d.fine) were used in the present work. All the solutions were prepared in doubly distilled water. A mixture of the solutions of the dye, glucose, sodium hydroxide was taken in an H-shaped glass cell. A platinum electrode (1.0 x 1.0 cm^2) was dipped into one limb of the cell and a saturated calomel electrode (SCE) was kept in the other. The platinum electrode was exposed to a 200W tungsten lamp (ECE) and the limb containing the SCE was kept in dark. A water filter was placed between the exposed limb and the light source to cut off infrared radiations.

The photochemical bleaching of safranine (Saf.) was studied potentiometrically. The photopotential and photocurrent generated by the system saf./glucose/OH^-/hν were measured by the digital pH meter (Agronic Model 511) and microammeter (Sympson), respectively. The i-V characteristics of the cell were studied using an external load (log 470K) in the circuit.

Results and Discussion

Effect of variation of pH

The electrical output of the cell was affected by the variation in pH of the system. The results are reported in Table-1

TABLE 1 : Effect of Variation of pH

[Saf.] = 4.00 x 10^{-6}M
Temp = 303 K

[Glucose] = 2.00 x 10^{-3} M
Light intensity = 10.4 mW cm^{-2}

pH	Photopotential (mV)	Photocurrent (μA)
12.0	280.0	31.0·
12.4	343.0	38.0
12.7	373.0	35.0
12.9	311.0	29.0
13.0	210.0	25.0

It is observed from table-1 that there is an increase in electrical output of the cell with the increase in pH values. At pH 12.7 a maximum was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the safranine glucose system were found to be quite sensitive to the pH of the solutions.

It was observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than its pKa value (pH > pKa). The reason may be the availability of reductant in its anionic form, which is a better donor form.

Effect of variations of [Glucose] concentration

The electrical output of the cell was affected by the variation of reducing agent concentration [glucose] in the system; the results are summarized in Table-2. Lower concentrations of reducing agents resulted in a fall in electrical output because fewer reducing agent molecules were available for electron donation to dye molecules.

TABLE 2 : Effect of Variation of [Glucose] concentration

[Saf.] = 4.00 x 10^{-6}M
pH = 12.7

Light intensity = 10.4 mW cm^{-2}
Temp = 303 K

	[Glucose] x 10^3M				
	1.5	1.8	2.0	2.3	2.6
Photopotential (mV)	261.0	327.0	373.0	313.0	241.0
Photocurrent (μ A)	25.0	40.0	35.0	31.0	24.0

Large concentration of reducing agent again resulted in a decrease in electrical output, because the large number of reducing agent molecules hinder the dye molecules reaching the electrode in the desired time limit.

Effect of variation of [Safranine] concentration

Dependence of photopotential and photocurrent on the concentration of dye was studied and the results are summarized in Table-3

TABLE 3 : Effect of Variation of [Safranine] concentration

[Glucose] = 2.00×10^{-3}M Light intensity = 10.4 mW cm^{-2}
pH = 12.7 Temp = 303 K

	[saf.] x 10^6 M				
	3.0	3.5	4.0	4.2	4.5
Photopotential (mV)	274.0	324.0	373.0	295.0	219.0
Photocurrent (μ A)	26.0	32.0	35.0	30.0	21.0

Lower concentration of dye resulted into a fall in photopotential and photocurrent because fewer dye molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. The greater concentration of dye again resulted in a decrease in electrical output as the intensity of light reaching the dye molecule near the electrode decreases due to absorption of the major portion of the light by dye molecules present in path.

Effect of diffusion path length

The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell was studied using H-cells of different dimension. The results are reported in table-4.

It was observed that there was a sharp increase in photocurrent i_{max} in the first few minutes of illumination and then there was a gradual decrease to a stable value of photcurrent. This photocurrent at equilibrium is represented as i_{eq}. This kind of photocurrent behaviour is an initial rapid reaction followed by a slow rate determining step at a later stage.

On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada (7), it may be concluded that the leuco or semi reduced form of dye, and the dye itself are the main electroactive species at the illuminated and the dark electrodes, respectively. However, the reducing agents and its oxidized products behave as the electron carriers in the cell diffusing through the path.

TABLE 4 : Effect of Diffusion Path Length

[Saf.] = 4.00×10^{-6}M
pH = 12.7
Temp = 303K

[Glucose] = 2.00×10^{-3}M
Light intensity = 10.4 mW cm^{-2}

Diffusion path length D_L (mm)	Maximum photocurrent i_{max} (μ A)	Equilibrium photocurrent i_{eq} (μ A)	Rate of initial generation of current (μ A min^{-1})
35.0	56.0	34.0	5.5
40.0	58.0	35.0	5.7
45.0	60.0	35.0	6.0
50.0	62.0	34.0	6.1
55.0	64.0	34.0	6.4

Current Voltage (i-V) characteristics of the cell.

The short circuit (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells were measured with a microammeter (circuit closed) and with a digital pH meter (circuit open), respectively. The current and potential value between these two extreme values (V_{oc}) and (i_{sc}) were recorded with a carbon pot (log 470 K) connected into microammeter through which an external load was applied.

It was observed that i-V curve deviated from its ideal regular rectangular shape. A point in i-V curve, called power point (pp) was determined where the product of potential and current was maximum. The values of potential as V_{pp} and i_{pp}, respectively. With the help of i-V curve, the fill factor was determined as 0.18 using the formula

$$\text{fill-factor} \quad (n) \quad = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \qquad (1)$$

Conversion efficiency and performance of the cell

With the help of current and potential values at power point and the incident power of radiations, the conversion efficiency of the cell was determined as 0.0356 % by using the formula

$$\text{Conversion efficiency} =- \frac{V_{pp} \times i_{pp}}{10.4\ (mW/cm^2)} \times 100\ \% \qquad (2)$$

The performance of the cell was studied by applying the external load necessary to have the current and potential at the power point after removing the source of light. It was observed that the cell can be used in the dark at its power point for 85 minutes.

Mechanism

On the basis of the above investigations, the mechanism of photocurrent generation in the photogalvanic cell can be represented as follows :

Illuminated Chamber

$$\mathrm{Saf} \xrightarrow{h\nu} \mathrm{Saf}^* \tag{3}$$

$$\mathrm{Saf}^* + \mathrm{R} \longrightarrow \mathrm{Saf}^- + \mathrm{R}^+ \tag{4}$$

At electrode

$$\mathrm{Saf}^- \longrightarrow \mathrm{Saf} + e^- \tag{5}$$

Dark Chamber

At electrode

$$\mathrm{Saf} + e^- \longrightarrow \mathrm{Saf}^- \tag{6}$$

$$\mathrm{Saf}^- + \mathrm{R}^+ \longrightarrow \mathrm{Saf} + \mathrm{R} \tag{7}$$

Where Saf, Saf^*, Saf^-, R and R^+ are the safranine, excited form of safranine, semi or leuco form of safranine, glucose and its oxidized form, respectively.

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