Full Length Research Paper

Tween 60 – amido black 10B – ascorbic acid system: Studies of photogalvanic effect and solar energy conversion

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Solar energy conversion and storage by use of photogalvanic cell was studied in Tween 60 – amido black – ascorbic acid system. Photogalvanic effect was studied in photogalvanic cell consisting of ascorbic acid as a reductant, Amido black 10B as photosensitizer and Tween 60 as surfactant in aqueous solution. The photopotential and photocurrent generated were 996.0 mV and 420 μA respectively. The observed power of the cell was 84.68 μW at its power point. The conversion efficiency and fill factor was determined as 1.62 and 0.38% respectively. The cell performance was 130 min. in dark. A mechanism for the photogeneration of electricity has also been proposed. The effect of different parameters (pH, diffusion length, electrode area, light intensity) on the electrical output of the cell were also been observed.

Key words: Photopotential, photocurrent, conversion efficiency, amido black 10B, Tween 60, ascorbic acid.

INTRODUCTION

The photogalvanic cell produces an electromotive force (voltage) upon absorbing photon. This cell works on photogalvanic effect. Rideal and Williams (1925) first of all reported the photogalvanic effect but it was systematically investigated by Rabinowitch (1940A and B). Later on this field get momentum by the work of some other workers (Hann et al., 1973; Clark and Eckert, 1975; Albery and Archer, 1977; Goldstein et al., 1980; Hamdi and Aliwi, 1996). Construction of a photogalvanic cell using photosynthetic reaction center complex and Cytochrome c2 from Rhodosprillium rubrum by Matsumoto et al. (2001). Progress in conversion of solar energy directly to electricity by means of the multilayer ion-thionine photo-galvanic system is). Spectral studies on the interaction of safarnine T, phloxin, fluorescien with inorganic ions their photogalvanic effect was studied by Ghosh and Bhattacharya (2002). Bisquert et al. (2004) have reviewed the physical chemical principal of dyesensi-tized solar cells, whereas Meyer (2005) has presented the molecular approaches to solar energy

conversion.

Singh and Mishra (2005) also reported studies of photochemical conversion. Photogalvanic studied for solar energy conversion in fuchsine basic-EDTA system reported by Ameta et al. (2006). Recently, some new photogalvanic systems with appreciable outputs reported using various dyes with surfactants (Meena and Singh, 2006; Chhagan Lal, 2007; Genwa and Mahaveer, 2008; Meena et al., 2009; Genwa et al., 2009; Genwa and Kumar, 2010; Yadav and Lal, 2011). Present system is the effort to observe the effect of neutral surfactant (Tween 60) on the electrical output of the cell in presence of Amido Black 10B as photosensitizer in photogalvanic cell for solar energy conversion.

MATERIALS AND METHODS

Amido Black 10B (LOBA Chemie pvt. Ltd, Mumbai), Tween 60 (LDH), Ascorbic acid (SISCO, Mumbai) and NaOH (RANKEM) were used in the present work. Structure and properties of Amido Black 10B, Tween 60 are shown Figure 1. All solutions were prepared by direct weighing in double distilled water and kept in amber cloured container to protect them from direct light. Photogalvanic effect of dye was studied using H- shaped glass tube which consist known amount of the solution of Amido Black 10B, Tween 60, Ascorbic acid, NaOH and distilled water so as to keep total volume of the

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$$Na^+$$
 $-O_3S$ $SO_3^ Na^+$ NO_2 NO_2

Figure 1. (a) Structure of Amido Black 10B; Solid crystalline black power, Molecular formula - $C_{22}H_{14}N_6Na_2O_9S_2$, Molecular weight - 616.49, Soluble in water, Maximum absorption (λ_{max}) - 610 nm (b) Tween 60 (Polyoxyethylene sorbitan monostearate); A pale yellow semisolid liquid, molecular formula - $C_{24}H_{46}O_6(C_2H_4O)_n$, Molecular weight - 1312, Soluble in water.

mixture always 25.0 ml. NaOH is used to maintained the pH of solution. A Platinum electrode (1.0×1.0 cm²) was dipped in one limb and a saturated calomel electrode (SCE) immersed in another limb of the H- tube. In present system, we have used two electrode system; platinum electrode as a working electrode and SCE as counter electrode. The terminals of the electrodes were then connected to a digital pH meter. The entire system was first placed in dark until a stable potential was reached, then the limb containing platinum electrode was exposed to the light source (projector Tungsten lamp). The light intensity was varied by employing tungsten lamp of different wattage. A water filter was placed between the illuminated chamber and the light source to cut off thermal radiations. The photochemical bleaching of dye (Amido Black 10B) were studied potentiometrically. Absorption spectra of dye-surfactant combination have been taken by using Systronics Spectrophotometer 106 with the matched pair of silica cuvetts (path length 1 cm). All spectral measurements were duplicated in a constant temperature water bath maintained with in ±1°C and mean values were processed for data analysis. Over all experimental setup of cell assembly (Genwa and Kumar, 2010) is shown in Figure 2.

RESULTS AND DISCUSSION

Absorption properties of Amido Black 10B - Tween 60

Amido black10b shows absorption peak (λ_{max}) in visible region with maximum at 610 nm. Maximum absorption

was recorded at Amido Black 10B - Tween 60 combination of concentration $1.1\times10^{-5}\,\mathrm{M} + 0.80\times10^{-3}\,\mathrm{M}$. The changes observed in the spectra shown in Figure 3.

Effect of variation of pH

Photogalvanic cell containing Amido Black 10B – Tween 60 – Ascorbic acid system was found to be quite sensitive to pH of the solution. The photopotential and photocurrent is increased with increase pH value (in alkaline range) of the cell. At pH 11.17, a maxima was obtained. On further increase in pH, there was a decrease photopotential and photocurrent. The optimum electrical output was obtained at particular pH value (11.17). It may be due to better availability of reductant's donor form at that pH value. The results showing the effect of pH are summarized in Table 1.

Effect of variation of dye (Amido Black 10B), surfactant (Tween 60), and reductant (Ascorbic acid) concentration

Results showing the effect of dye, surfactant and reductant concentration are given in Table 2. It was observed that the

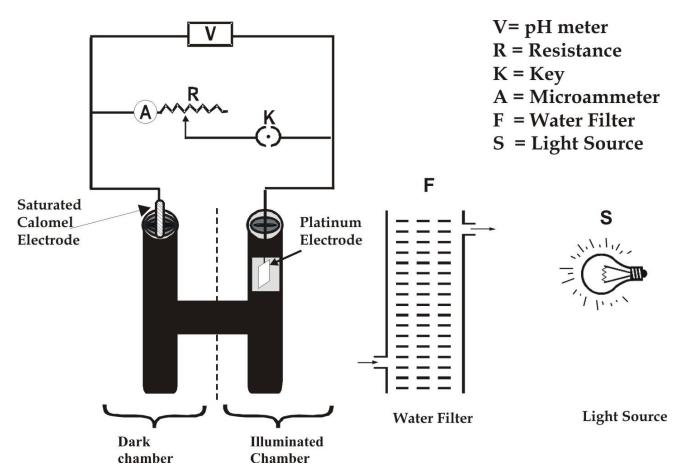


Figure 2. Set up of photogalvanic cell assembly.

photopotential and photocurrent of Amido Black 10B -Ascorbic acid system for the better performance of the photogalvanic cell proper concentration of dye was needed. The Photopotential and photocurrent increased with increase in Amido Black 10B concentration. A maxima was obtained at certain dye concentration $(1.1 \times 10^{-5} \text{ M})$. On further increase in the concentration of dye, a fall in the electrical output was observed. At the lower concentration range of dye, there are only a few dye molecules to absorb the major portion of the light and therefore, there was a low electrical output, while higher concentration of dye again resulted in a decrease in electrical output due to intensity of light reaching the molecule near the electrode decrease due to absorption of the major portion of the light by the dye molecules present in the path, therefore corresponding fall in the electric output of the cell.

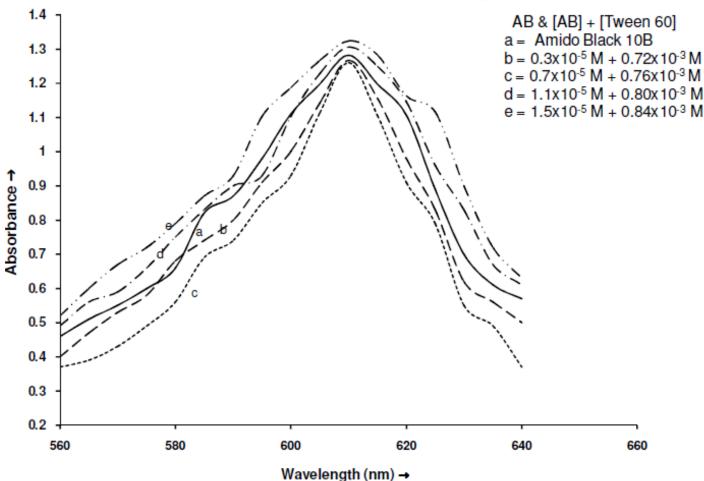
Tween 60 was used as a Surfactant in the system. The photopotential and photocurrent of the cell was increased on increasing the concentration of Tween 60 reaching a maximum value at 0.8×10^{-3} M. On further increase in Tween 60 concentration, a fall in electrical output of cell was observed. Most important properties of surfactants (miceller systems) are the ability to solubilize a variety of

molecules and substantial catalytic effect on chemical reaction in the cell.

The electrical output of the cell was affected by the variation of reductant (ascorbic acid) concentration. It was observed that photopotential and photocurrent was found to increase to maximum value and then decrease in electrical output because fever reductant molecules were available for electron donation to dye molecules. Higher concentration of reductant again resulted in a decrease in electrical output, because large numbers of reductant molecules hinders the dye molecule reaching close to electrode in the desired time limit.

Effect of diffusion length and electrode area

The diffusion length is the distance between the two electrodes in H-Cell. The effect of variation of diffusion length on the current parameters of the cell (i_{max} , i_{eq}) and initial rate of generation of photocurrent are studied using H-Shaped cell of different diameters. i_{max} found to increase with diffusion length. It is observed that in the first few minutes of illumination there is sharp increase in the photocurrent. The conductivity of electroactive species



Tween 6 0 - Amido black 10B - Ascorbic acid System

Figure 3. Absorption spectrum of dye and Dye + Surfactant.

Table 1. Effect of pH.

рН	Photopotential (mV)	Photocurrent (µA)
11.09	812	334
11.13	884	385
11.17	996	420
11.21	943	407
11.25	892	386

 $^{^{}a}$ Tween 60 = 0.80 × 10 $^{-3}$ M, b Amido Black 10B = 1.1 × 10 $^{-5}$ M, c Ascorbic Acid = 1.72 ×10 $^{-3}$ M, d Light Intensity = 10.4 mW cm $^{-2}$, e Temp. = 303 K

depends on its population between electrodes. As diffusion length increased, the volume of dye solution and intern population of dye molecule(Amido Black 10B) increased leading higher i_{max} the electroactive nature of dye/dye is provide by the fact that i_{max} increase with diffusion length. There for it may be concluded that the main electro active species are the leuco or semi form of dye- and the dye in the illumination and the dark chamber

respectively. The reductant its oxidation products act only as electron carriers in the path the result are summarized in Table 3.

Effect of light intensity

The effect of light intensity was studied by using tungsten

Concentration	Photopotential(mV)	Photocurrent(µA)
	[Amido Black 10B] × 10 ⁻⁵ M	· ·
0.3	794	295
0.7	902	389
1.1	996	420
1.5	882	381
1.9	775	309
	[Tween 60] × 10 ⁻³ M	
0.72	758	248
0.76	889	366
0.80	996	420
0.84	865	329
0.88	780	279
	[Ascorbic acid] × 10 ⁻³ M	
1.64	715	238
1.68	891	356
1.72	996	420
1.76	860	284
1.80	810	231

Table 2. Effect of variation of Amido Black 10B, Tween 60, ascorbic acid concentration.

Table 3. Effect of diffusion length.

Diffusion length D _L (mm)	Maximum Photocurrent i _{max} (μA)
50	477
55	489
60	500
65	511
70	522

^aTween 60 = 0.80×10^{-3} M, ^bAmido Black 10B = 1.1×10^{-5} M, ^cAscorbic Acid = 1.72×10^{-3} M, ^dLight Intensity = 10.4 mW cm⁻², ^eTemp. = 303 K, ^fpH = 11.17

lamps of different wattage. It was observed that photocurrent showed a linear increasing behavior with the increase in light intensity whereas photopotential increase in logarithmic manner. This increasing behavior of electrical output with increase in light intensity was due to increase in number of photons with increase in light intensity, The observed results showing dependence of light intensity on photopotential and photocurrent of the cell are reported in Figure 4.

Current – voltage (i-V) characteristics

The open circuit voltage (V_{oc}) and short circuit current (i_{sc}) of the photogalvanic cell were measured under the continuous illumination of light, with the help of digital pH meter (keeping the circuit open) and a micro ammeter (keeping the circuit closed), respectively. The potential and current in between this two extreme values (V_{pp} and i_{pp}) were recorded with the help of a carbon pot (log 407K) connected in the circuit of micro ammeter, through

which an external load applied on it. i-V characteristics of the cell containing Amido Black 10B – Tween 60 – Ascorbic acid system is shown as a curve in Figure 5. It was observed that i-V curve deviated from its regular rectangular shape. A point in the i-V curve, called power point (pp), was determined where the product of current and potential was maximum. With the help of i-V curve, the fill-factor was calculated as 0.38 using the formula:

Fill-factor (ff) =
$$\frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}}$$
 (1)

Storage capacity (Performance) and conversion efficiency of the cell

The performance was determined in term of $t_{1/2}$ i.e. the time required in fall of the power output to its half at power point in dark. It was obtained with time-power curve

^aLight Intensity = 10.4 mW cm⁻², ^bTemp. = 303 K, ^cpH = 11.17.

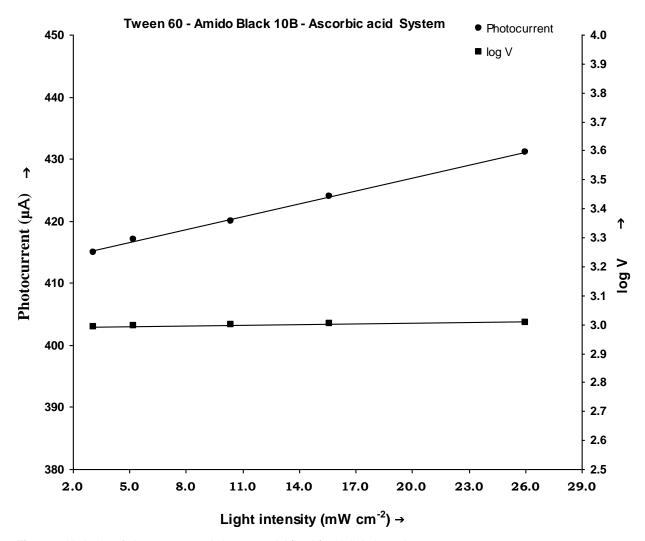


Figure 4. Variation of photocurrent and photopotential (log V) with light intensity.

(Figure 6). It was observed that the cell can be used in dark at its power point for 130 min using Amido Black 10B – Tween 60 – Ascorbic acid system in photogalvanic cell. The conversion efficiency of the cell was determined as 1.62% using the formula:

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

where, V_{pp} , i_{pp} and A are the potential at power point, current at power point and electrode area, respectively.

Role of Surfactant (Tween 60)

The surfactant head can be charged (anionic or cationic), dipolar (zwitterionic), or non-charged. The Tween 60 has non charged head (neutral). The micellization is the

important property of surfactant, by this surfactant are able to solubilize a variety of molecules and substantial catalytic effect on many chemical reactions (Fendler and Fendler, 1975). Photoinduced electron transfer processes in miceller system are potentially important for efficient energy conversion and storage due to surfactant micelles help to achieve the separation of photoproducts by the hydrophilic- hydrophobic interaction of the products with the micellar interface (Genwa and Sonel, 2009). Dye has tendency of interacting with surfactant micelle of opposite charges. In the opposite charge dye and surfactant, a strong dye-surfactant complex is formed in which dye molecule is surrounded by surfactant micelles in some regular geometry which retards the intermolecular twisting resulting in an enhancement of fluorescence. Groenen et al. (1984) studied an Iron-thionin photogalvanic cell with addition of neutral micelles (TX-100), Jana (2000) studied the molecular interaction of Phenazine dyes in aqueous solution of Triton X-100 and observed that dye form charge transfer or electron-doner-

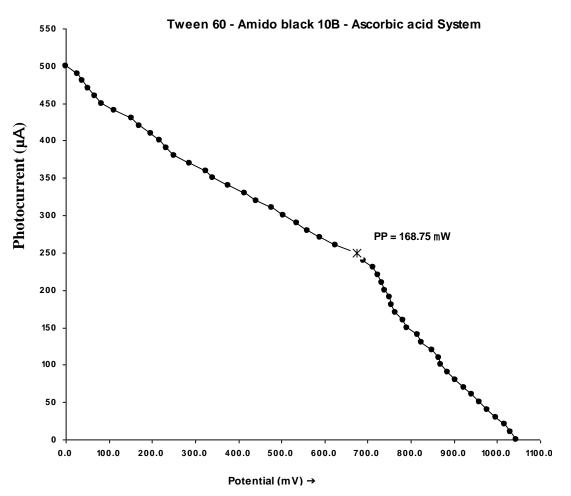


Figure 5. Current – potential (i-V) curve of the cell.

acceptor complex with surfactant (Triton X-100).

Mechanism

When certain dyes are excited by the light in the presence of electron donating substance (reductant), the dyes are rapidly changed into colorless form. The dye now acts as on powerful reducing agent and can donate electron to other substance and reconverted to its oxidised state (Oster, 1962). On the basis of earlier studies, a tentative mechanism in the photogalvanic cell may be proposed as follows:

Illuminated chamber

On irradiation, dye molecule get excited:

$$\begin{array}{ccc} D & \longrightarrow & D^* & \text{(1)} \\ \text{Ground state} & \text{First excited state} \end{array}$$

The excited dye molecule accepts an electron from

reductant and converted into semi or leuco form of dye, and the reductant into its excited state:

$$D^* + R \longrightarrow D^-(\text{semi or leuco}) + R^+$$
 (2)
Triplet state

At platinum electrode

The semi or leuco form of dye loses an electron and converted into original dye molecule:

$$D \rightarrow D + e^{-}$$
 (3)

Dark chamber

At counter electrode:

$$D + e^{-} \longrightarrow D^{-}$$
 (semi or leuco) (4)

Finally leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule and the cycle will go on:

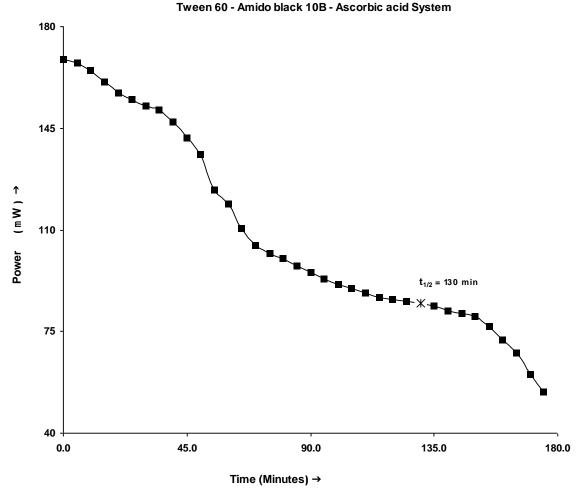


Figure 6. Time-power curve of the cell.

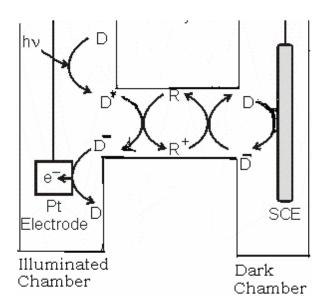


Figure 7. Schematic diagram of cell reaction mechanism. SCE=saturated Calomel Electrode. D=Dye (Photosensitizer). R=Reductant. ē=Electron.

$$D^{-} + R^{+} \longrightarrow D + R \tag{5}$$

Where D, D*, D*, R and R* represents the dye, its excited form, reduced form of dye, reductant and its oxidized form respectively. Schematic representation of mechanism is shown in Figure 7.

Conclusions

The photogalvanic conversion of solar energy has attracted attention of scientists towards solar energy conversion and storage. This cell undergoes cyclical charging and discharging process. The charging of cell occurs only in presence of illuminating source. The discharging of cell takes place only when we apply the external circuit for electron transfer. As long as there is no external circuit, the cell will keep light energy stored. The photogalvanic cell have inbuilt storage capacity and stored energy can be used in absence of light where as photovoltaic cells needs extra hardware as batteries for energy storage, photogalvanic cells are economic than

photovoltaic cells because low cost materials are used in these cells. The Conversion efficiency, storage capacity and fill factor are recorded as 1.62%, $t_{1/2}130$ min. and 0.38 respectively in Tween 60 – Amido Black 10B – Ascorbic acid system. These values of electrical outputs are more than values reported (0.048,17 min, and 0.24) in system with neutral surfactant Tween 80 (Gangotri et al., 1994) present work has given an impetus to explore the more suitable selection of surfactant, reductant and photosensitizer in order to its practical implementation.

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