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Photoelectrochemical Effect in Dye Sensitized Solar Cell: Cetyltrimethylammonium Bromide–Bromothymol Blue– Oxalic Acid System

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ABSTRACT:
To achieve the conversion efficiency of photogalvanic cell the photogalvanic effect in photoelectrochemical cells, using Cetyl ammonium bromide as surfactant, Bromothymol blue as photosensitizer, and Oxalic acid as electron donor, was experimentally investigated. Different standard H-cell configurations were set-up by varying the combination of electrolyte. Long-term open-circuit voltage measurements were conducted in order to check the constancy of the cells. The conversion efficiency, power at power point, photopotential and photocurrent generated by this cell were 0.25%, 26.25μW, 615.0mV and 142μA, respectively. The effect of various parameters likes dye concentration, pH, reductant concentration etc. on the electrical output of the cell has been studied. Performance of the cell was determined in dark at its power point.

KEYWORDS: Photopotential, Photocurrent, Cetyl ammonium bromide, Diffusion Length.
Nomenclature

V_{dark}	Dark potential (mV)	V_{oc}	Open circuit voltage (mV)
V_{max}	Maximum voltage (mV)	ΔV	Photopotential (mV)
i_{max}	Maximum current (μA)	P_{pp}	Power at power point (μW/m^2)
V_{pp}	Power point voltage (mV)	i_{pp}	Power point current (μA)
FF	Fill factor	CE	Conversion efficiency (%)
$t_{1/2}$	Storage capacity (min)	CTAB	Cetyltrimethylammonium bromide
i_{sc}	Short circuit current (μA)	i_{eq}	Equilibrium current (μA)

1. INTRODUCTION:

Solar energy provides clean abundant energy and is therefore best option for an environmentally friendly energy source in future. Solar cells are devices that are able to convert solar energy into electrical energy. The aim of solar cell research is to increase the solar energy conversion efficiency at low cost to provide a cost-effective sustainable energy source [1].

The burning of fossil fuels introduces many harmful pollutants into the atmosphere and contributes to environmental problems like global warming and acid rain, solar energy is completely non-polluting [2]. Environmentally it is one of the least destructive of all the sources of energy. Practically, it can be adjusted to power nearly everything except transportation with very little adjustment and even transportation with some modest modifications to the current general system of travels. Clearly solar energy is a resource of the future [3].

Photoelectrochemical effect is defined as a change in the electrode potential (in open circuit) or in the current flowing (in close circuit) in an electrode/electrolyte system on irradiation [4]. Photogalvanic cell is a Photoelectrochemical device in which light is absorbed by a highly absorbing electrolyte solution to provide energy for a reaction [5]. Electrical energy is generated by subsequent transfer of charge to electrode by a photoreduced or photooxidized molecule diffusing from the bulk of the electrolyte. This device is in principle, perhaps closest of the PEC devices for photosynthesis. Hoffman and Lichtin[6] have discussed various problems encountered in the development of this field. M. Inglot et.al.[7] studied enhanced photogalvanic effect in graphene.

Researchers have recently reported some better photogalvanic systems for solar energy conversion and storage by using different combinations of Photosensitizer-Reductant-Surfactant in photoelectrochemical cells.

From the literature survey [8-22], it was observed that no attention has been paid to intensification of efficiency and commercial viability of the photoelectrochemical solar cells / photogalvanic cells. Therefore this work is undertaken.

2. EXPERIMENTAL WORK:

We used Double distilled water for preparation of solutions and all the stock solutions prepared by direct weighing and kept in amber coloured vessels to protect them from direct light. H-shaped glass tube is used as cell vessel. A total 25.0 ml volume of the mixture of known concentration of the solutions of photosensitizer (Bromothymol Blue), Sodium hydroxide, surfactant, oxalic acid as reductant, and double distilled filled in H-cell. 1.0 x 1.0 cm^2 dimension platinum electrode is dipped in one arm and a Saturated Calomel Electrode (SCE) is immeresed in the other arm of the H tube. The electrodes are then connected to a digital pH meter- Systronics Model – 335 and the entire setup was first placed in dark till a constant potential was obtained, then the platinum electrode was exposed to a 200 W tungsten lamp (Philips). A water filter was used to cut off infrared radiations. The photochemical bleaching of Bromothymol blue was studied potentiometrically. A microammeter (INCO Model No. 65) was used to measure the potential and current generated by the cell.

3. OBSERVATIONS, RESULTS AND DISCUSSIONS:

3.1 OBSERVATIONS OF CURRENT WITH TIME:

Iniatially a rapid rise in photocurrent of CTAB –Bromothymol Blue–Oxalic Acid System on illumination and reaches a maximum within few minutes. This maximum value of current is denoted by i_{max}. Then the current is found to decrease gradually with the period of illumination finally reaching a constant value at equilibrium. This value is represented as i_{eq}. The current was decreased on withdrawing the source of illumination. The Variations of current with respect to time in this system is given in Table 1.

Table 1: Observations **of Photocurrent with Time**

[CTAB] = 7.00 x 10^{-4} M Intensity of Light = 10.4 $mWcm^{-2}$
[BTB] = 4.00 x 10^{-5} M Temp. = 303 K
[Oxalic Acid] = 3.00 x 10^{-3} M pH of system = 12.8

Time (Minutes)	Photocurrent (μ A)
0.0	0.0
2.0	25.0
5.0	60.0
10.0	105.0
20.0	120.0

30.0	136.0
40.0	142.0
50.0	140.0
60.0	135.0
70.0	133.0
80.0	130.0
90.0	125.0
100.0	122.0
110.0	120.0
120.0	115.0
130.0	110.0
140.0	105.0
150.0	100.0
155.0	95.0
160.0	95.0
165.0	95.0
170.0	95.0
180.0	**95.0(Light off)**
190.0	82.0
200.0	75.0

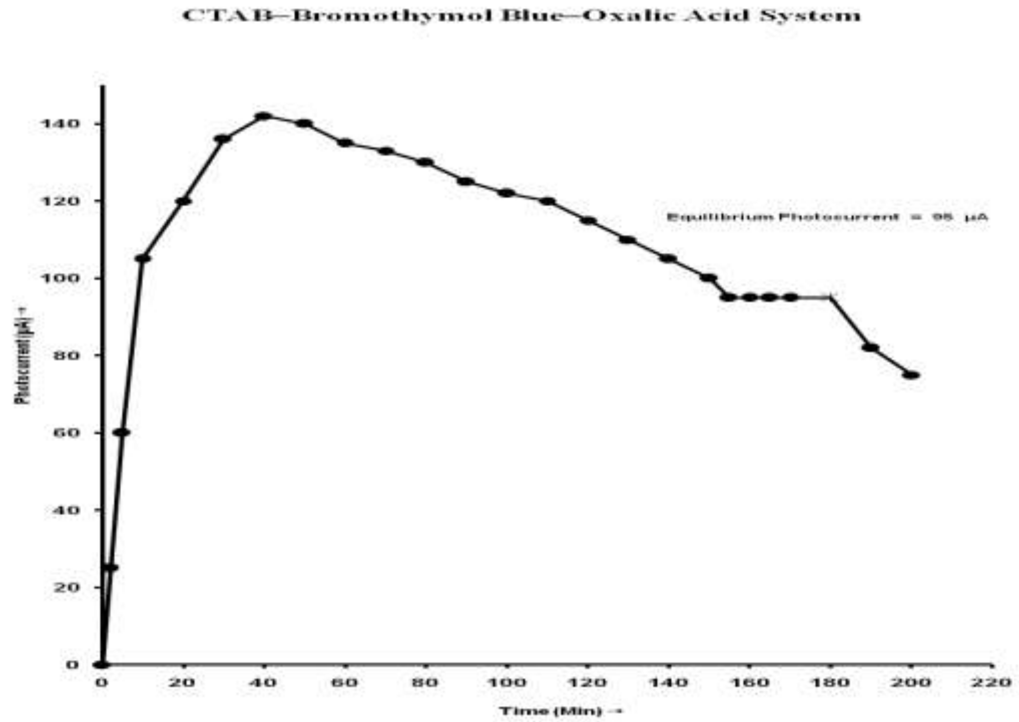

FIG.1. OBSERVATION OF PHOTOCURRENT WITH TIME:

3.2 STUDY THE EFFECT OF VARIATIONS OF pH OF THE SYSTEM:

The effect of variations of pH on photopotential and photocurrent are reported in table-2. Cell containing Cetyl ammonium bromide – Bromothymol Blue – Oxalic Acid System is found to be very sensitive to the pH of the solutions. An increase in the electrical output with the increase in pH value (in the alkaline range) is observed. At pH 12.8 a maximum output is obtained and on further increase in pH, there is a decrease in electrical output.

Table 2: Study on Variations of pH of the system

[CTAB] = 7.00 x 10^{-4} M Intensity of Light = 10.4 $mWcm^{-2}$
[BTB] = 4.00 x 10^{-5} M Temp. = 303 K
[Oxalic Acid] = 3.00 x 10^{-3} M

CTAB–Bromothymol Blue–Oxalic Acid System	pH of the System				
	12.0	12.4	12.8	13.0	13.4
Photopotential (m V)	430.0	501.0	615.0	523.0	444.0
Photocurrent (μ A)	48.0	64.0	95.0	70.0	49.0
Power (μ W)	20.64	32.06	58.43	36.61	21.76

3.3 STUDY THE EFFECT OF VARIATIONS OF CETYL AMMONIUM BROMIDE CONCENTRATION:

It was viewed that the electrical yield of the cell rises with rise in the concentration of surfactant (CTAB) upto arriving at the extreme value and on further rise in their concentration; the photopotential, photocurrent and power of photogalvanic cell were begin to tumble down. Effect of Variations of concentration of surfactant (CTAB) is given in Table-3

Table 3: Effect of Variations of surfactant [CTAB] Concentration

[CATB] = 4.00 x 10^{-5} M Temp. = 303 K
[Oxalic Acid] = 3.00 x 10^{-3} M pH of system = 12.8
Intensity of Light = 10.4 $mWcm^{-2}$

CTAB–Bromothymol Blue–Oxalic Acid System	[CTAB]] x 10^{4} M				
	5.0	6.0	7.0	8.0	9.0
Photopotential (m V)	444.0	509.0	615.0	533.0	424.0
Photocurrent (μ A)	44.0	60.0	95.0	71.0	41.0
Power (μ W)	19.54	30.54	58.43	37.84	17.38

3.4 EFFECT OF VARIATIONS OF [OXALIC ACID] CONCENTRATION:

With raising the concentration of the reductant i.e. Oxalic-Acid the photo-potential raises till it touches a maximum value and on extra rise the concentration of Oxalic-Acid, electrical output of the cell was a decreased. The effect of variations of the Oxalic Acid concentration on the electrical yield of CTAB – Bromothymol Blue–Oxalic acid cell is reported in Table 4.

Table 4: Effect of Variations of [Oxalic Acid]

[CTAB] = 7.00 x 10^{-4} M Intensity of Light = 10.4 $mWcm^{-2}$
[BTB] = 4.00 x 10^{-5}M Temp. = 303 K
pH of system = 12.8

CTAB–Bromothymol Blue–Oxalic Acid System	[Oxalic Acid] x 10^{3} M				
	2.5	2.8	3.0	3.2	3.5
Photopotential (m V)	400.0	449.0	615.0	483.0	424.0
Photocurrent (μ A)	34.0	45.0	95.0	61.0	41.0
Power (μ W)	13.60	20.21	58.43	29.46	17.38

3.5 EFFECT OF BROMOTHYMOL BLUE CONCENTRATION:

It was observed that the increase in electrical productivity (i.e. photopotential and photocurrent) with the increased of the concentration of dye (BTB). In these Variations a maxima was attained at specific concentration of Bromothymol Blue, beyond this decline in the electrical productivity (i.e. photopotential and photocurrent) of the cell is observed. These effects of Variations of Bromothymol Blue concentration on electrical productivity (i.e. photopotential and photocurrent) are given in Table-5.

Table 5: Effect of Variations of [Bromothymol Blue]

[CTAB] = 7.00 x 10^{-4} M Intensity of Light = 10.4 $mWcm^{-2}$
[Oxalic Acid] = 3.00 x 10^{-3}M Temp. = 303 K
PH of system = 12.8

CTAB–Bromothymol Blue–Oxalic Acid System	[BTB] x 10^{5} M				
	3.6	3.8	4.0	4.2	4.4
Photopotential (mV)	423.0	500.0	615.0	510.0	401.0
Photocurrent (μA)	40.0	58.0	95.0	66.0	34.0
Power (μW)	16.92	29.00	58.43	33.67	13.63

3.6 CURRENT-POTENTIAL (I-V) PLOTS OF THE SYSTEM:

Short circuit current (i_{sc}) is measured by microammeter in close circuit and open circuit voltage (Voc) measured by pH meter in open circuit. By the help of a pot (carbon, log 470 K) an external load was applied on microammeter joined to circuit and recorded the extreme value in between the potential and current values. Results of CTAB -Bromothymol Blue–Oxalic-Acid cell for i-v characteristics is reportrd in table 6.

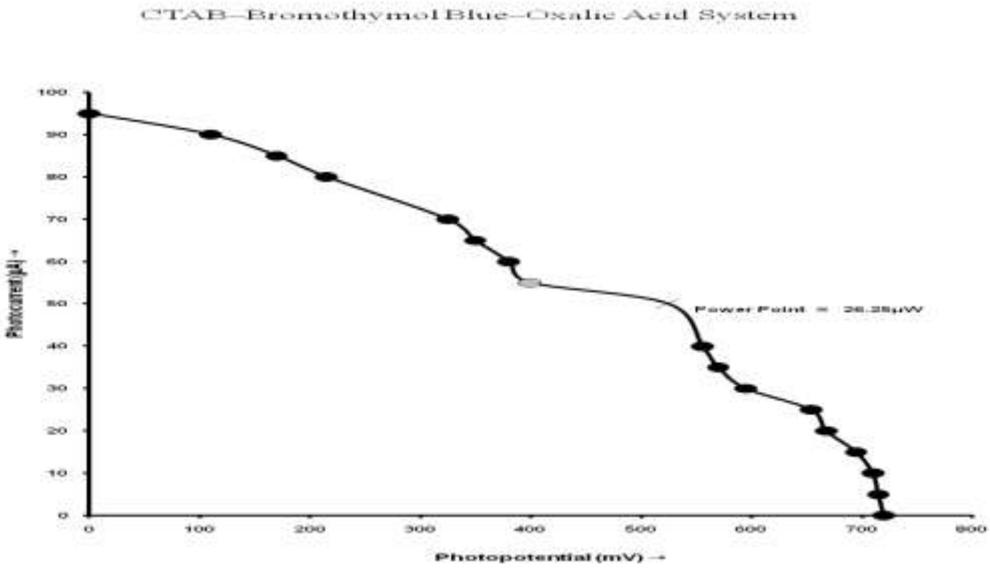

FIG.2- CURRENT- VOLTAGE (I-V) CURVE OF THE CELL

In this i-V curve we found that it deviates from regular rectangular shape. A point in i-V curve where the product of current and potential is maximum, called Power Point (PP) and the fill-factor is calculated at power point by using the formula :

$$\text{Fill factor } (\eta) = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \qquad \ldots\ldots\ldots(1)$$

3.7 STORAGE CAPACITY (PERFORMANCE) OF THE CELL:

The storage capacity or performance of the system is perceived by applying an exterior load (required to have current at power point) after swiching off the illumination as soon as the potential ranges a constant value. The storage capacity or performance of the system is determined in terms of $t_{½}$ (it is the time taken in fall of the power output to its half at power point in dark). It is detected that the Cetyl ammonium bromide Blue–Oxalic Acid system can be used in dark for 73.0 minutes**.** The graphical representation of outcomes is given in figure 2.

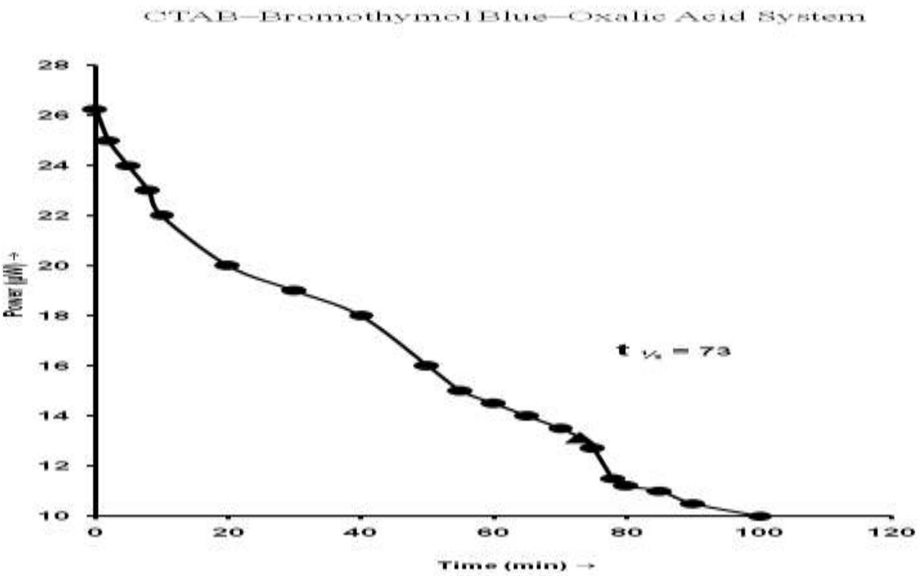

FIG.3- PERFORMANCE OF THE CELL

3.8 CONVERSION EFFICIENCY OF THE CELL:

By using current and potential values at Power Point (pp) and the incident power of radiations, the conversion efficiency of the cell is calculated by usinf following formula. The conversion efficiency of the system is 0.25 %

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

4. CONCLUSION:

In present study of photoelectrochemical cell of various system combinations we have reached upto a good output and by using surfactant-reductant-photosensitizer conversion efficiency, storage capacity and other electrical parameters were improved and stability of system also enriched. The commercially viable systems are still likely to be discovered. This kind of solar cell will be economical viable and pollution free and can be handle easy. The efforts must made to rise electrical out-put by picking appropriate material to reach the preferred results for commercial sustainability of the photogalvanic cells to decrease the energy crisis in some extent.

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