# USE OF DYES IN PHOTOGALVANIC CELLS FOR SOLAR ENERGY CONVERSION AND STORAGE : THYMOLE BLUE AND ASCORBIC ACID SYSTEM

## R. C. MEENA[∗], VIJAY KUMAR and GAUTAM SINGH

Department of Chemistry, Jai Narain Vyas University, JODHPUR – 342005 (Raj.) INDIA

## ABSTRACT

The photovoltages developed in system consisting of thymole blue as photosensitizer and ascorbic acid as reducing agent. The photopotential and photocurrent generated by this cell were 810.00 mV and 150.0 μA, respectively. The observed conversion efficiency was 0.8038% and the maximum power of cell was 82.06 μW. The storage capacity of the cell was 54.00 minutes in dark. The effects of different parameters on electrical output of the cell were observed and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cell.

**Key words:** Thymole blue, Ascorbic acid, Fill factor, Conversion efficiency, Power point, Storage capacity.

## INTRODUCTION

The conversion of solar energy in electrical energy in solar cell has attracted attention of scientists for the solution of power crisis. The photogalvanic effect was reported first of all by Becquerel[1,2] and systematically investigated by Rideal and Williams[3] and by the Rabinowitch[4] in iron-thionine system. Later on, it was investigated by many workers from time to time.

The photogalvanic effect was reported by Clark and Eckert[5] but it was systematically investigated by Suda et al.[6] and Hall et al.[7]. Later on, Rohatgi Mukherjee et al.[8-12] have reported some interesting photogalvanic systems. Theoretical conversion efficiency of photogalvanic cell is about 18% but the observed conversion efficiencies are quite low due to low stability of dyes, back-electron transfer, aggregation of dye molecules around electrode, etc.

---

[∗] Author for correspondence; Warden Residence Engg. Hostel No. 4, PWD Road, Jodhpur –11 Rajasthan INDIA; E-mail : rcmeena007@rediffmail.com

A detailed literature[13-28] survey reveals that different photosensitizers and reductants have been used in photogalvanic cells, but no attention has been paid to use of the thymol blue as photosensitizer and ascorbic acid as reductant in the photogalvanic cell for solar energy conversion and storage. Therefore, the present work was undertaken.

## EXPERIMENTAL

Thymole blue (LOBA), ascorbic acid (LOBA) and sodium hydroxide (s.d.fine) were used in the present work. All the solutions were prepared in doubly distilled water and were kept in amber coloured containers to protect them from sunlight. A mixture of solution of thymol blue, ascorbic acid and sodium hydroxide was taken in an H-type glass tube. A platinum electrode (1.0 x 1.0 cm$^2$) was immersed into one arm of the H-tube and a saturated calomel electrode (SCE) was kept in the other. The whole system was first placed in dark till a stable potential was obtained and then, the arm containing the SCE was kept in dark, and the platinum electrode was exposed to a 200 W tungsten lamp. A water filter was used to cut off infra-red radiations. The photochemical bleaching of thymol blue was studied potentiometrically. A digital pH meter (Agronic Model 511) and a microammeter (OSAW, India) were used to measure the potential and current generated by the system, respectively.

## RESULTS AND DISCUSSION

**Effect of pH**

**Table 1. Effect of pH**

| [Thymole blue]= $4.8 \times 10^{-6}$ M | | | [Ascorbic acid] = $6.00 \times 10^{-3}$M | | |
| --- | --- | --- | --- | --- | --- |
| Temp. = 303 K | | | Light intensity = 10.4mW cm$^{-2}$ | | |
| | **pH** | | | | |
| | 12.3 | 12.6 | 12.9 | 13.2 | 13.5 |
| Photopotential (mV) | 774.0 | 795.0 | 810.0 | 798.0 | 777.0 |
| Photocurrent ($\mu$A) | 120.0 | 135.0 | 150.0 | 136.0 | 118.0 |
| Power ($\mu$W) | 72.05 | 78.04 | 82.06 | 80.05 | 76.07 |

The electrical output of the cell was affected by the variation in pH of the solution of system. It can be observed from Table 1 or Fig.1 that there is an increase in electrical output of the cell with the increase in pH, values. At pH = 12.9, a maxima was obtained.
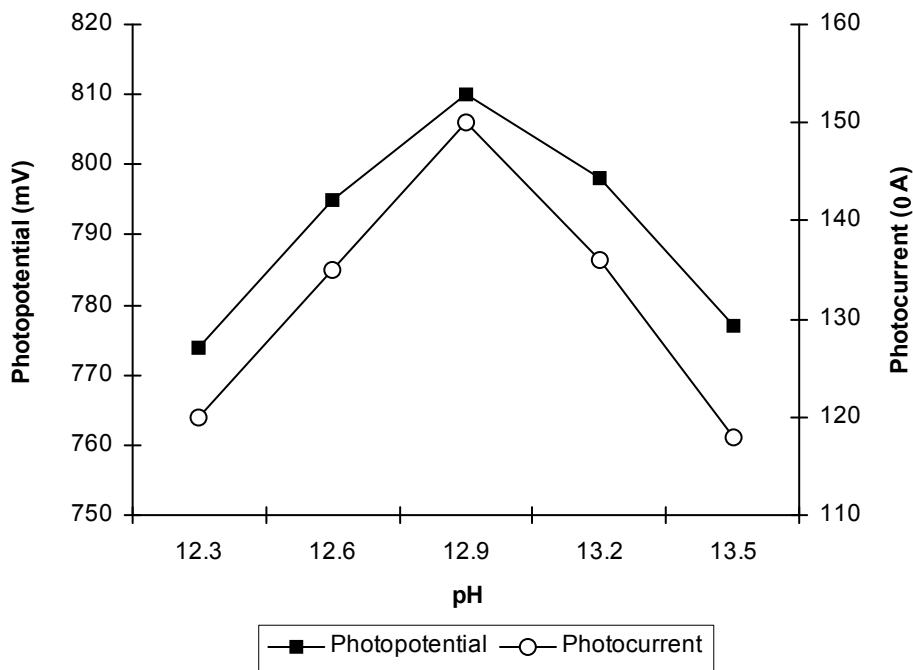
**Fig. 1: Variation of photopotential and photocurrent with pH**

On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the thymol blue and ascorbic acid system were found to be quite sensitive to the pH of the solution of the system.

It was observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher then 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 ascorbic acid concentration

The electrical output of the cell was affected by the variation of reducing agent concentration [Ascorbic acid] in the system. The results are summarized in Table 2 and graphically represented in Fig. 2.

**Table 2. Effect of ascorbic acid concentration**

| [Thymole blue] = $4.8 \times 10^{-6}$ M | | | Light intensity = 10.4 mW cm$^{-2}$ | | |
|---|---|---|---|---|---|
| pH = 12.9 | | | | Temp. = 303 K | |

| | [Ascorbic acid] $\times 10^3$M | | | | |
|---|---|---|---|---|---|
| | 4.4 | 5.2 | 6.0 | 6.8 | 7.4 |
| Photopotential (mV) | 724.0 | 764.0 | 810.0 | 774.0 | 737.0 |
| Photocurrent ($\mu$A) | 106.0 | 125.0 | 150.0 | 133.0 | 112.0 |
| Power ($\mu$W) | 74.04 | 79.08 | 82.06 | 77.06 | 73.02 |
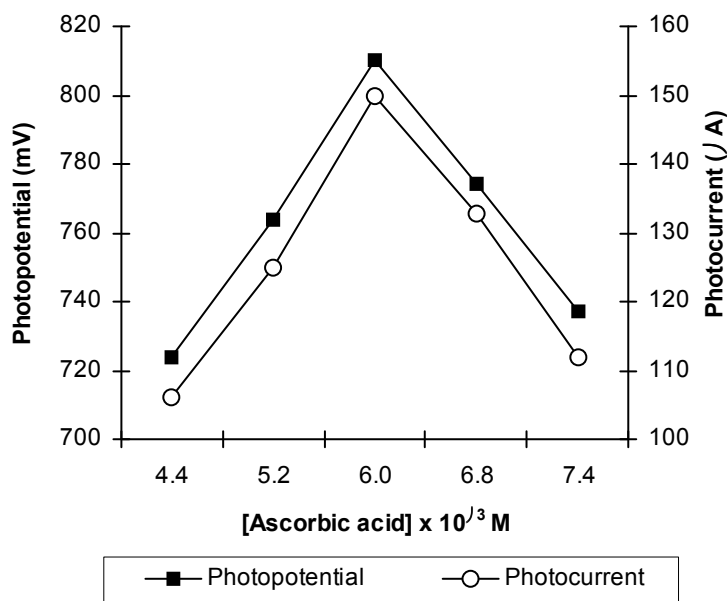


**Fig. 2: Variation of photopotential and photocurrent with ascorbic acid concentration**

Lower concentrations of reducing agents resulted into a fall in electrical output because fewer reducing agent molecules were available for electron donation to thymol blue molecules.

Larger concentrations of reducing agent again resulted into 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 thymol blue concentration**

Dependence of photopotential and photocurrent on the concentration of thymole blue was studied and the results are summarized in Table 3 and graphically represented in Fig. 3.

**Table 3.** **Effect of thymol blue concentration**

| [Ascorbic acid] = $6.00 \times 10^{-3}$ M | | | Light intensity = 10.4 mW cm$^{-2}$ | | |
|---|---|---|---|---|---|
| pH = 12.9 | | | | Temp. = 303 K | |
| | **[Thymole blue]** $\times 10^6$ **M** | | | | |
| | 1.6 | 3.2 | 4.8 | 6.4 | 8.0 |
| Photopotential (mV) | 771.0 | 790.0 | 810.0 | 788.0 | 767.0 |
| Photocurrent ($\mu$A) | 115.0 | 135.0 | 150.0 | 132.0 | 114.0 |
| Power (μW) | 75.04 | 77.08 | 82.06 | 74.07 | 73.06 |
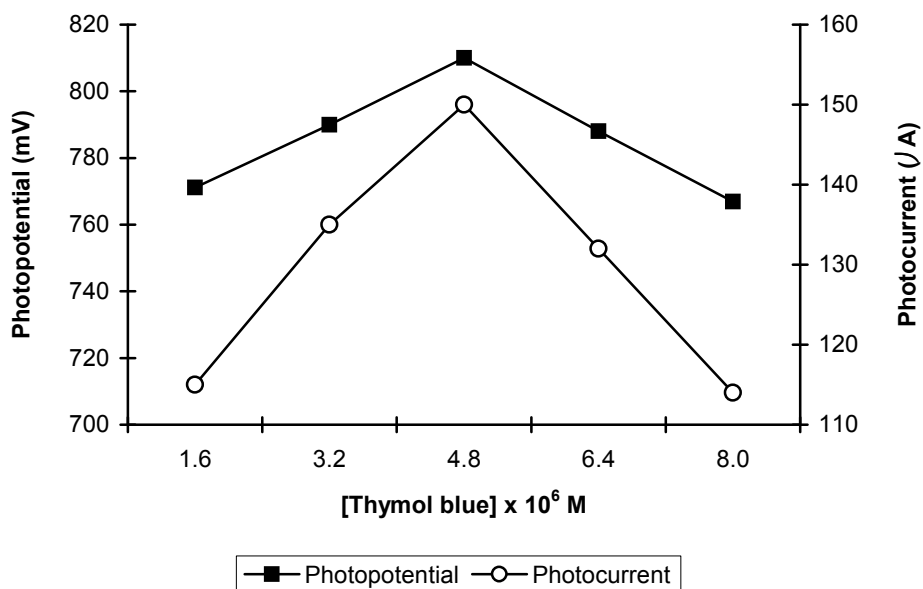


**Fig. 3: Variation of photopotential and photocurrent with thymol blue concentration**

Lower concentration of dyes resulted into a fall in photopotential and photocurrent

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

**Effect of diffusion 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 dimensions. The results are reported in Table 4 and graphically represented in Fig. 4.

**Table 4.** **Effect of diffusion length**

| [Thymole blue] = $4.8 \times 10^{-6}$ M | | [Ascorbic acid]= $6.00 \times 10^{-3}$ M | |
| pH = 12.9 | | Light intensity = 10.4 mW cm$^{-2}$ | |
| | | Temp. = 303 K | |

| Diffusion path length DL (mm) | Maximum photocurrent $i_{max}$ (μA) | Equilibrium photocurrent $i_{eq}$ (μA) | Rate of initial generation of current (μA min$^{-1}$) |
| --- | --- | --- | --- |
| 35.0 | 180.0 | 130.0 | 12.7 |
| 40.0 | 182.0 | 140.0 | 14.2 |
| 45.0 | 184.0 | 150.0 | 15.8 |
| 50.0 | 186.0 | 150.0 | 17.4 |
| 55.0 | 190.0 | 167.0 | 19.1 |

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 photocurrent. This photocurrent at equilibrium is represented as $i_{eq}$. This kind of behaviour of photocurrent indicates that there is an initial rapid reaction followed by slow rate determining step at a later stage.

On the basis of the effect of diffusion path length on the current parameters, as investigated earlier by Kaneka and Yamada[29], it may be concluded that the leuco- or semi reduced form of dyes, 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.
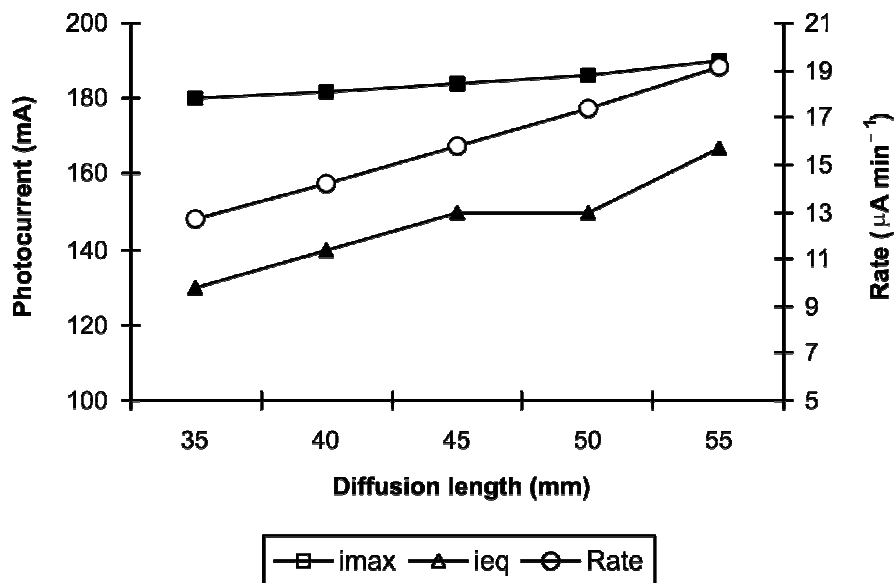


**Fig. 4: Variation of current parameters with diffusion length**

## Current-voltage (i-V) charateristics and conversion efficiency

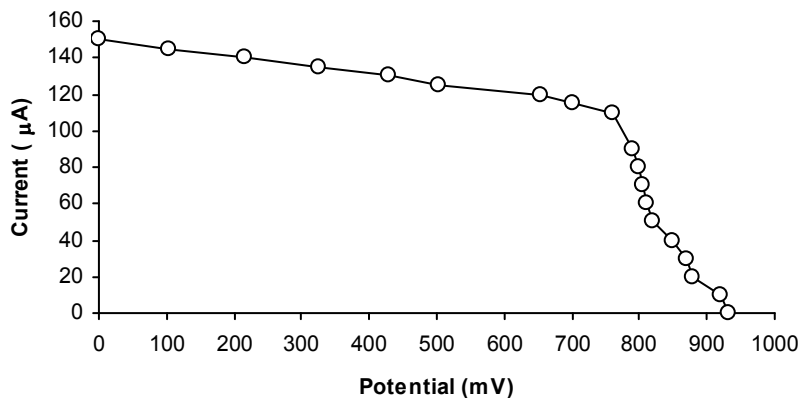It was observed that i-V curve of the cell deviated from its regular rectangular shape (Fig. 5).



**Fig. 5: i-V characteristic of the cell**

A point in i-V curve, called the power point (pp) was determind, where the product of potential and current was maximum. With the help of i-V curve, the fill factor and conversion efficiency of the cell were determined as 0.49 and 0.8038%, respectively using the following formula-

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

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

Where $V_{pp}$, $i_{pp}$, $V_{oc}$, $i_{sc}$ are the potential at power point, current at power point, open circuit voltage and short circuit current, respectively. The system (at its optimum condition ) was exposed to sunlight.

**Electroactive species**

Various probable processes may by considered for the photocurrent generation in photogalvanic cells. The results of the effect of diffusion length on current parameters were utilized to know more about the electroactive species. The possible combinations for electroactive species in photogalvanic cell are tabulated in Table 5.

**Table 5. Possible combinations for electroactive species**

| In illuminated chamber | In dark chamber |
| --- | --- |
| TB | Oxidized form of reductant ($R^+$) |
| Leuco or Semi - TB$^-$ | Oxidized form of reductant ($R^+$) |
| Leuco or Semi - TB$^-$ | TB |

The oxidized form of the reductant is formed only in the illuminated chamber and if it is considered to be the electroactive species in the dark chamber, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. As a consequence, the maximum photocurrent ($i_{max}$) and rate of increase in photocurrent should decrease with an increase in diffusion length, but this was not observed experimentally. The $i_{eq}$ was also observed to be independent with respect to change in diffusion length (rather, it decreases slightly). Therefore, it may be concluded that the main electroactive species are the leuco- or semi-TB and the dye TB in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products act only as
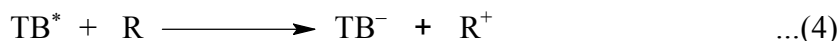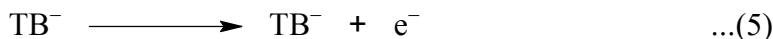
electron carrier in the path.

## Mechanism

On the basis of the above investigations, the mechanism of photocurrent generation in the photogalvanic cell can be proposed as follows:
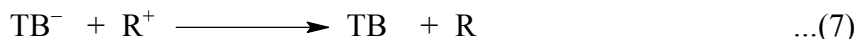
**Illuminated chamber**

**Bulk solution**

$$TB \xrightarrow{h\nu} TB^* \qquad ...(3)$$

$$TB^* + R \longrightarrow TB^- + R^+ \qquad ...(4)$$

**At electrode**

$$TB^- \longrightarrow TB^- + e^- \qquad ...(5)$$

**Dark chamber**

**At electrode**

$$TB + e^- \longrightarrow TB^- \qquad ...(6)$$

**Bulk solution**

$$TB^- + R^+ \longrightarrow TB + R \qquad ...(7)$$

Where TB, $TB^-$, R and $R^+$ are the thymole blue and its leuco- or semi-leuco forms, reductant and its oxidized form, respectively.

## CONCLUSION

The performance of the cell was studied by applying an external load necessary to maintain current and potential at the power point after removing the source of light until the output (power) drops to its half value at the power point in the dark. It was observed that the cell can be used in the dark at its power point for 54.0 minutes.

## ACKNOWLEDGEMENT

## REFERENCES

1.   K. Bacquerel, C. R. Acad Sci., Paris. **9,** 14 (1839).

2.   K. Bacquerel, C. R. Acad Sci., Paris. **9,** 561(1839).

3.   E. K. Redial and D. C. Willians, J. Chem. Soc., 258 (1925)

4.   E. Rabinowitch, J. Chem. Phys., **8**, (1940), 551

5.   W. D. K. Clark and J. A. Eckert, Solar Energy **17**, 147-152 (1975).

6.   Y. Suda, Y. Shimoura, T. Sakata, and H. Tsubomura, J. Chem. Phys., **82**, 268-271 (1978).

7.   D. E. Hall, W. D. K. Clark, A. Eckert, N. N. Litchin and P. D. Wildes, Am. Ceram. Soc. Bull., **56**, 408-411 (1977).

8.   K. K. Rohtagi- Mukherjee, M. Bagchi and B. B. Bhowmik, Electrochim Acta., **28**, (1983), 293-300.

9.   K. K. Rohtagi- Mukherjee, M. Roy and B. B. Bhowmik, Solar Energy, **4**, 417-419 (1983).

10.   K. K. Rohtagi- Mukherjee, S. Roy and B. B. Bhowmik, Indian J. Chem., **25A**, 714-718 (1986).

11.   K. K. Rohtagi- Mukherjee, M. Bagchi and B. B. Bhowmic, Indian J. Chem., **24A**, 1002-1007 (1985).

12.   K. K. Rohtagi- Mukherjee, S. Roy and B. B. Bhowmik, Indian J. Chem., **24A**, 5-7 (1985).

13.   B. B. Bhowmik, S. Roy and K. K. Rohtagi- Mukherjee, Indian J. Technol., **24**, 388-390 (1986).

14.   B. B. Bhowmik, S. Roy and K. K. Rohtagi- Mukherjee, Indian J. Chem., **26A**, 183-186 (1987).

15.   M. Matsumura, Y. Nomura and H. Tsubomura, Bull. Chem. Soc. Jpn., **49**, 1409-1410 (1976).

16.   T. Osa and M. Fujihara, Nature **264**, 349-350 (1976).

17. T. Watanabe, A. Fujishima, O. Tatsushi and K. Honda, Bull. Chem. Soc. Jpn., **49**, 8-11 (1976).

18. M. Fujihara, M. Ohishi and T. Osa, Nature, **268**, 226-228 (1977).

19. W. D. K. Clark and N. Sutin, J. Am. Chem. Soc., **99**, 4676-4682 (1977).

20. A. Fujishima, T. Iwase and K. Honda, J. Am. Chem. Soc., **98**, 1625-1627 (1976).

21. M. T. Spitler and M. Calvin, J. Chem. Phys., **66**, 4294-4305 (1977).

22. M. Nakao, T. Watanabe and K. Honda, Chem. Lett., **2**, 225-226 (1984).

23. M. Eisenberg and H. P. Silvermann, Electrochim Acta, 1-12 (1961).

24. K. M. Gangotri and R. C. Meena, J. Photochem. Photobiol. A Chem., **123**, 93-97 (1999).

25. K. M. Gangotri and R. C. Meena, J. Photochem. Photobiol. A Chem., **141**, 175-177 (2001).

26. K. M. Gangotri, R. C. Meena and Gautam Singh, Afinidad, J. **59**, 501 (2003).

27. R. C. Meena and Gautam Singh, J. Chem. Sci., **116**, 179-184 (2004).

28. R. C. Meena and R. S. Sindal, Int. J. Chem. Sci., **2(3),** 321-330 (2004).

29. Kaneka and Yamada, J. Phys. Chem., **81**, 1213 (1977).