USE OF SURFACTANT IN PHOTOGALVANIC CELL FOR SOLAR ENERGY CONVERSION AND STORAGE : TWEEN–80–OXALIC ACID–TOLUIDINE BLUE SYSTEM

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ABSTRACT

Photogalvanic effect was studied in photogalvanic cell containing tween–80 as micellar species, oxalic acid as reductant and toluidine blue as photosensitizer. The photopotential and photocurrent generated were 268.0 mV and 51.0 µA, respectively. The observed conversion efficiency was 0.0687% and the maximum power of cell was 6.30 µW. The storage capacity of the cell was 8.0 minutes in dark. The effect of different parameters on electrical output of the cell was observed and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cells.

Keywords : Tween–80, Photogalvanic cells, Toluidine blue, Oxalic acid, Surfactant

INTRODUCTION

The photogeneration of electricity has attracted attention of scientists as a viable media for solar energy conversion with bright future prospects. Becquerel[1,2] first observed in 1839 the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was first of all reported by Rideal and Williams[3] but it was systematically investigated by Rabinowitch[4,5]. Later on Kaneka and Yamada[6], Murthy *et al.*[7], Rohtagi Mukherjee *et al.*[8], Ameta *et al*[9–11] and Gangotri *et al.*[12–14] have reported some interesting photogalvanic systems. Theoretical conversion efficiency of photogalvanic cells is about 1.8% but the observed conversion efficiencies are quite low due to low stability of dyes, back electron transfer, aggregation due to molecules around electrodes etc. Hoffman and Lichtin[15] have discussed various problems encountered in the development of this field.

A detailed literature[16–31] survey reveals that different photosensitizers and reductants have been used in photogalvanic cells, but no attention has been paid to use tween–80–toluidine blue – oxalic acid system in the photogalvanic cell for solar energy conversion and storage. Therefore, the present work was undertaken.

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EXPERIMENTAL

Tween–80 (LOBA), oxalic acid (LOBA), toluidine blue (LOBA) and sodium hydroxide (s.d. fine) were used in 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 solutions of tween–80, toluidine blue and sodium hydroxide was taken in a H–type glass tube. A platinum electrode (1.0 x 1.0 cm^2) was immersed into one arm of 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. Then the arm containing platinum electrode was exposed to a 200 W tungsten lamp. A water–filter was used to cut off infrared radiations. The photochemical bleaching of toluidine blue was studied potentiometrically. A digital pH meter (Agronic Model 511) and a micro–ammeter (OSAW, India) were used to measure the potential and current generated by the system, respectively.

RESULTS AND DISCUSSION

Effect of [Tween–80] concentration

It was observed that electrical output of the cell was found to increase on increasing the concentration of surfactant (micellar species) reaching a maximum value. On further increase in their concentration, fall in photopotential, photocurrent and power of the photogalvanic cell was observed. The results are summarized in Table 1.

Table 1. Effect of Tween–80 concentration

[Toluidine blue] = 3.20 x 10^{-5} M   [Oxalic acid] = 8.00 x 10^{-4} M

pH = 11.4   Light intensity = 10.4 mWcm^{-2}

Temperature = 303 K

	[Tween–80] x 10^3 M				
	0.92	1.20	1.60	2.00	2.50
Photopotential (mV)	145.0	162.0	180.0	178.0	160.0
Photocurrent (μA)	25.0	30.0	36.0	33.0	29.0
Power (μW)	3.62	4.86	6.48	5.87	4.64

Effect of pH

The electrical output of the cell was affected by the variation in pH of the system. It was observed (Table 2), that there is an increase in electrical output of the cell with the increase in pH values. At pH 11.4, a maxima was obtained. On further increase in pH, there was a decrease

in photopotential and photocurrent. Thus, photogalvanic cells containing the tween–80–toluidine blue–oxalic acid system were found to be quite sensitive to the pH of the solutions.

Table 2. Effect of pH

[Toluidine blue] = 3.20 x 10^{-5} M   [Tween–80] = 1.60 x 10^{-3} M

[Oxalic acid] = 8.00 x 10^{-4} M

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

	pH				
	10.8	11.0	11.4	11.5	11.6
Photopotential (mV)	103.0	161.0	180.0	159.0	115.0
Photocurrent (μA)	18.0	30.0	36.0	29.0	15.0
Power (μW)	1.85	4.83	6.48	4.61	1.72

Effect of oxalic acid concentration

The electrical output of the cell was affected by the variation of reducing agent concentration in the system. The results are summarized in Table 3.

Lower concentrations of reducing agents resulted in a fall in electrical output because less number of reducing agent molecules were available for electron donation to dye molecules.

Table 3. Effect of oxalic acid concentration

[Toluidine blue] = 3.20 x 10^{-5} M   [Tween–80] = 1.60 x 10^{-3} M

Light intensity = 10.4 mWcm^{-2} pH = 11.4

Temperature = 303 K

	[Oxalic Acid] x 10^4 M				
	7.00	7.50	8.00	8.50	9.00
Photopotential (mV)	140.0	170.0	180.0	148.0	131.0
Photocurrent (μA)	26.0	29.0	36.0	31.0	24.0
Power (μW)	3.64	4.93	6.48	4.58	3.14

Larger concentration 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 toluidine blue concentration

Dependence of photopotential and photocurrent on the concentration of dye was studied and the results are summarized in Table 4.

Lower concentrations 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 into a decrease in electrical output as the intensity of light reaching the dye molecules near the electrode decreases due to absorption of the major portion of the light by dye molecules present in path.

Table 4. Effect of toluidine blue concentration

[Oxalic Acid] = 8.00×10^{-4} M   [Tween–80] = 1.6×10^{-3} M

pH = 11.4   Light intensity = 10.4 mWcm^{-2}

Temperature = 303 K

	[Toluidine Blue] x 10^5 M				
	2.00	2.50	3.20	3.50	4.00
Photopotential (mV)	151.0	171.0	180.0	160.0	138.0
Photocurrent (µA)	29.0	33.0	36.0	30.0	22.0
Power (µW)	4.37	5.64	6.48	4.80	3.03

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 5. It was observed that there was a sharp increase in photocurent 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 photocurrent behaviour indicates 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[6], 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 5. Effect on diffusion length

[Toluidine blue] = 3.20 x 10^{-5}M   [Tween–80] = 1.6 x 10^{-3} M

[Oxalic Acid] = 8.00 x 10^{-4} M

pH = 11.4   Light intensity = 10.4 mWcm^{-2}

Temperature = 303 K

Diffusion path length D_1 (mm)	Maximum photocurrent i_{max} (µA)	Equilibrium photocurrent i_{eq} (µA)	Rate of initial generation of current (µ A min^{-1})
35.0	44.0	36.0	8.5
40.0	45.0	36.0	8.7
45.0	46.0	35.0	9.2
50.0	47.0	34.0	9.6
55.0	47.0	34.0	9.8

Current–voltage (i–V) characteristics and conversion efficiency

It was observed that i–V curve of the cell deviated from its regular rectangular shape as given in the Figure 1.

A point in 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, fill factor and the conversion efficiency of cell were determined as 0.44 and 0.0687%, respectively using the following formula –

$$\text{Fill Factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}}$$

$$\text{Conversion Efficiency} = \frac{V_{pp} \times i_{pp}}{10.4 \text{ mWcm}^{-2}} \times 100\%$$

Where V_{pp}, i_{pp}, V_{oc} and 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. The conversion data for the photogalvanic cell is reported in Table 6.
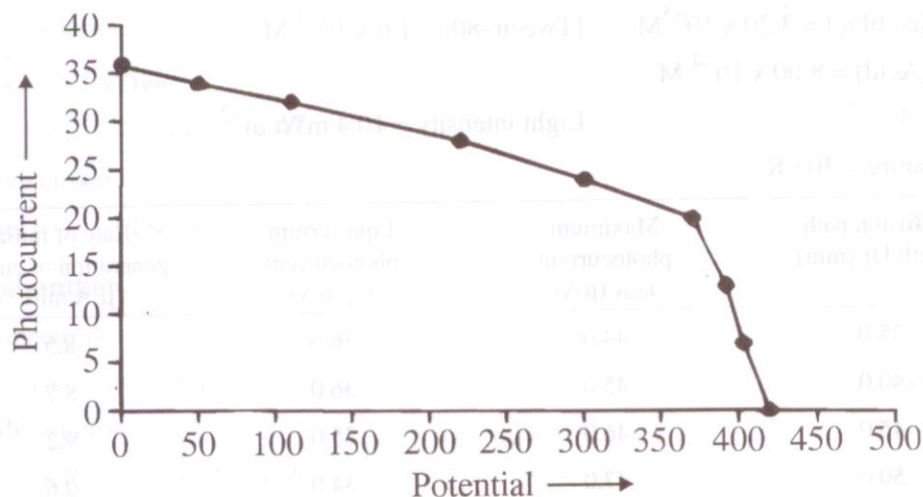
Fig. 1. Current-Voltage (i-V) curve of the cell

Table 6. Conversion efficiency and Sunlight conversion data

[Tween–80] = 1.60 x 10^{-3} M [Oxalic Acid] = 8.00 x 10^{-4} M [Toluidine blue] = 3.20 x 10^{-5} M, pH = 11.4; Temperature = 303 K Light Intensity = 10.4 mWcm^{-2}	Conversion Efficiency (%)	Sunlight Conversion Data	
		Photopotential (mV)	Photocurrent (μA)
Without micelle	0.0343	252.0	43.0
Tween–80	0.0687	268.0	51.0

Cell performance

The performance of the photogalvanic cell was studied by applying an external load necessary to maintain current at the power point after removing the source of light until the output (power) falls to its half value in dark. It was observed that the cell can be used in dark for 8 minutes.

Role of micelles

The usefulness of micelles[28] in photogalvanic cells with respect to their nature have been investigated and found to follow the order anionic micelle > neutral micelle > cationic micelle. Alkaties et al.[29] have studied the photoejection of electron from dye–surfactant system suggesting tunneling of photoelectrons from micellar phase to aqueous phase

whereas Mukhopadhya and Bhowmik[30] have suggested a probability of some charge transfer between micelle and the dye.

The photogalvanic cell containing toluidine blue and oxalic acid (without micelles) shows the conversion efficiency 0.0343% whereas the tween–80 (micelles) have increased the conversion efficiency i.e. 0.0687% of the photogalvanic cells. Tween–80 solubilises the dye more easily and stabilizes the system and may increase the probability of charge transfer between micelle and the dye in the system.

Electroactive species

Various probable processes may be 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 of electroactive species in photogalvanic cell are tabulated in Table 7.

Table 7. Possible combinations for electroactive species

In Illuminated Chamber	In Dark Chamber
Dye	Oxidized form of reductant (R^+)
Leuco or Semi–Dye$^-$	Oxidized form of reductant (R+)
Leuco or Semi–Dye$^-$	Dye

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 value 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–toluidine blue and the dye toluidine blue in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products act only as electron carriers in the path.

MECHANISM

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

Illuminated chamber

Bulk solution

$$Dye \xrightarrow{h\nu} Dye^*$$ ...(i)

$$Dye^* + R \longrightarrow Dye^- + R^+$$

At electrode

$$Dye^- \longrightarrow Dye + e^-$$ ...(iii)

Dark chamber

At electrode

$$Dye + e^- \longrightarrow Dye^-$$ ...(iv)

Bulk solution

$$Dye^- + R^+ \longrightarrow Dye + R$$ ...(v)

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

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