

Studies of surfactants in photogalvanic cells – NaLS-EDTA and azur-B system

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Abstract. Photogalvanic effects were studied in photogalvanic cells containing sodium lauryl sulphate as surfactant, EDTA as reductant and azur-B as photosensitizer. The photopotential and photocurrent generated were 814.0 mV and 255.0 mA respectively. The observed conversion efficiency was 1.2% and the maximum power of cell was 207.57 mW. The storage capacity of the cell was 26.0 min in dark. The effect of different parameters on electrical output of the cell was observed. A mechanism has been proposed here for the generation of photocurrent in photogalvanic cells.

Keywords. Sodium lauryl sulphate; fill factor; conversion efficiency; power point.

1. Introduction

The photogeneration of electricity has attracted the attention of scientists as viable media for solar energy conversion and storage in photogalvanic cells with bright future prospects.

The photogalvanic effect was first of all reported by Rideal and Williams¹ but it was systematically investigated by Rabinowitch^{2,3}. Becquerel^{4,5} first observed in 1839 the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. Thereafter, Kaneka and Yamada⁷, Murthy *et al.*,⁸ Rohtagi Mukherjee *et al.*,⁶ Ameta *et al.*^{9–11} and Gangotri *et al.*^{12–14} have reported some interesting photogalvanic systems. The theoretical conversion efficiency of photogalvanic cells is about 18% but the observed conversion efficiencies are quite low owing the low stability of azur-B, back electron transfer, aggregation of azur-B molecules around electrodes etc. Hoffman and Lichtin¹⁵ have discussed various problems encountered in the development of this field.

A detailed literature^{16–33} survey reveals that different photosensitizers and EDTA have been used in photogalvanic cells, but no attention has been paid to use of the NaLS-azur-B system in the photogalvanic cell for solar energy conversion and storage. The present work was undertaken to study this system.

2. Experimental

NaLS (SD Fine-Chem Limited) and sodium hydroxide (SD Fine) were used in the present work. All the solutions were prepared in doubly distilled water and kept in amber coloured containers to protect them from sunlight. A mixture of solutions of NaLS, azur-B and sodium hydroxide was taken in an H-shaped glass tube. A platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) was immersed into one arm of an 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 the SCE was kept in the dark, while the platinum electrode was exposed to a 200W tungsten lamp. A water-filter was used to cut off infrared radiations. The photochemical bleaching of azur-B was studied potentiometrically. A digital pHmeter (Agronic Model 511) and a micro-ammeter (OSAW, India) were used to measure the potential and current generated by the system respectively.

3. Results and discussion

3.1 Effect of variation of sodium lauryl sulphate concentration

It is observed that electrical output of the cell increases on increasing the concentration of NaLS (surfactant), reaching a maximum value. On further

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increase in concentration, fall in photopotential, photocurrent and power of the photogalvanic cell is seen, as is summarized in table 1.

3.2 Effect of variation of pH

The electrical output of the cell is affected by variation in pH of the system. It is observed from table 2 that there is an increase in electrical output of the cell with the increase in pH values. At pH 12.78 a maxima is obtained. On further increase in pH, there is decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the NaLS-EDTA-azur-B system are quite sensitive to the pH of the solutions.

It is observed that the pH for the optimum condition has a relation with pK_a of the reductant and the desired pH is higher than its pK_a value ($pH > pK_a$).

The reason may be the availability of reductant in its anionic form, which is a better donor form.

3.3 Effect of variation of EDTA concentration

The electrical output of the cell is affected by the variation of concentration of reducing agent (EDTA) in the system. These results are summarized in table 3.

Lower concentration of reducing agents results in fall in electrical output because fewer reducing agent molecules are available for electron donation to dye molecules.

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

Table 1. Effect of variation of cetyl trimethyl ammonium bromide concentration.

[Azur-B] = 4.96×10^{-5} M; [EDTA] = 2.24×10^{-3} M; pH = 12.78; light intensity = 10.4 mW cm^{-2} ; temp = 303 K.

| Parameters | [NaLS] $\times 10^{-3}$ M | | | | |
|---------------------|---------------------------|-------|-------|--------|-------|
| | 7.2 | 6.8 | 6.4 | 6.0 | 5.6 |
| Photopotential (mV) | 753.0 | 792.0 | 814.0 | 593.0 | 470.0 |
| Photocurrent (mA) | 275.0 | 300.0 | 300.0 | 100.0 | 110.0 |
| Power (mW) | 188.0 | 205.0 | 207.0 | 129.65 | 137.6 |

Table 2. Effect of variation of pH.

[Azur-B] = 4.96×10^{-5} M; [NaLS] = 6.40×10^{-3} M; [EDTA] = 2.24×10^{-3} M; temp. = 303 K; light intensity = 10.4 mW cm^{-2}

| Parameters | pH | | | | |
|---------------------|-------|-------|--------|-------|-------|
| | 12.83 | 12.80 | 12.78 | 12.74 | 12.71 |
| Photopotential (mV) | 593.0 | 784.0 | 838.0 | 337.0 | 301.0 |
| Photocurrent (mA) | 100.0 | 275.0 | 275.0 | 100.0 | 85.0 |
| Power (mW) | 29.65 | 132.6 | 175.98 | 168.5 | 21.07 |

Table 3. Effect of variation of EDTA concentration.

[Azur-B] = 4.96×10^{-5} M; [NaLS] = 6.4×10^{-3} M; light intensity = 10.4 mW cm^{-2} ; pH = 12.78; temp. = 303 K

| Parameters | [EDTA] $\times 10^{-3}$ M | | | | |
|---------------------|---------------------------|-------|-------|-------|-------|
| | 2.32 | 2.28 | 2.24 | 2.20 | 2.16 |
| Photopotential (mV) | 155.0 | 593.0 | 837.0 | 307.0 | 198.0 |
| Photocurrent (mA) | 100.0 | 100.0 | 300.0 | 50.0 | 75.0 |
| Power (mW) | 11.62 | 29.65 | 217.0 | 82.89 | 99.0 |

3.4 Effect of variation of azur-B (dye) concentration

Dependence of photopotential and photocurrent on the concentration of azur-B (dye) was studied and the results are summarized in table 4.

Lower concentration of dye result into 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 also results in 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 the path.

3.5 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-type cells of different dimension. The results are reported in table 5.

It was observed that there is sharp increase in photocurrent i_{\max} in the first few minutes of illumination and then there is a gradual decrease to a stable value of photocurrent. This photocurrent at equi-

librium 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 Yamada⁷ 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 carries in the cell diffusing through the path.

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

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

A point on the i – V curve called the power point (PP) is determined where the product of potential and current is maximum. The value of potential and current at the power point are represented as V_{PP} and i_{PP} respectively. With the help of the i – V curve the fill factor and the conversion efficiency of cell are determined as 0.45 and 1.20% respectively, using the following formulae

Table 4. Effect of variation of azur-B (dye) concentration.

[EDTA] = 2.24×10^{-3} M; [NaLS] = 6.4×10^{-3} M; light intensity = 10.4 mW cm^{-2} ; pH = 12.78; temp. = 303 K

| Parameter | [Azur-B] $\times 10^{-5}$ M | | | | |
|---------------------|-----------------------------|-------|-------|-------|-------|
| | 5.12 | 5.04 | 4.96 | 4.92 | 4.88 |
| Photopotential (mV) | 317.0 | 728.0 | 838.0 | 657.0 | 593.0 |
| Photocurrent (mA) | 50.0 | 285.0 | 300.0 | 100.0 | 50.0 |
| Power (mW) | 95.1 | 182.0 | 208.0 | 29.65 | 99.25 |

Table 5. Effect of diffusion length.

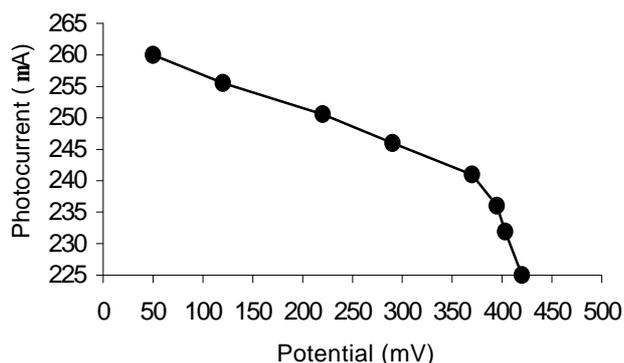
[Azur-B] = 4.96×10^{-5} M; [NaLS] = 6.4×10^{-3} M; [EDTA] = 2.24×10^{-3} M; pH = 12.78; temp. = 303 K; light intensity = 10.4 mW cm^{-2}

| Diffusion path length D_L (mm) | Maximum photocurrent i_{\max} (mA) | Equilibrium photocurrent i_{eq} (mA) | Rate of initial generation of current (mA min ⁻¹) |
|----------------------------------|--------------------------------------|---|---|
| 35.0 | 275.0 | 250.0 | 54.2 |
| 40.0 | 300.0 | 255.0 | 58.8 |
| 45.0 | 300.0 | 260.0 | 60.3 |
| 50.0 | 100.0 | 270.0 | 56.6 |
| 55.0 | 110.0 | 250.0 | 52.2 |

Table 6. Conversion efficiency and sunlight conversion data.

[Azur-B] = 4.96×10^{-5} M; [EDTA] = 2.24×10^{-3} M; [NaLS] = 6.40×10^{-3} ; pH = 12.78; temp. = 303 K; light intensity = 10.4 mW cm^{-2}

| Conditions | Conversion efficiency (%) | Sunlight conversion data | |
|---------------------|---------------------------|--------------------------|-------------------|
| | | Photopotential (mV) | Photocurrent (mA) |
| Without micelle | 0.32 | 755.0 | 110.0 |
| In presence of NaLS | 1.20 | 814.0 | 255.0 |

**Figure 1.** Current–voltage (i – V) curve of the cell.**Table 7.** Possible combination for electroactive species

| In illuminated chamber | In dark chamber |
|------------------------|--------------------------------------|
| Azur-B | Oxidized form of reductant (R^+) |
| Leuco or semi azur-B | Oxidized form of reductant (R^+) |
| Leuco or semi azur-B | Azur-B |

$$\text{fill factor} = (V_{PP} \times i_{PP}) / (V_{oc} \times i_{sc}),$$

$$\text{conversion efficiency} = (V_{PP} \times i_{PP}) / (10.4 \text{ mWcm}^{-2}) \times 100\%,$$

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.

3.7 Cell performance

The performance of the cell was studied by applying the external load necessary to maintain current and potential at the power point after removing the

source of light until the output (power) reduces 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 26.0 min.

4. Role of micelles

The utility of surfactants²⁸ in photogalvanic cells with respect to their nature has been investigated and found to follow the order – anionic surfactants > neutral surfactants > cationic surfactants. Alkatie et al²⁹ have studied the photoejection of electrons from dye-surfactant systems, suggesting the tunneling of photoelectrons from the micellar phase to the aqueous phase, whereas Mukhopadhaya and Bhowmik³⁰ have suggested the probability of some charge transfer between surfactant and dye.

Photogalvanic cells containing azur-B and EDTA (without micelles) show a conversion efficiency of 0.32%, and addition of sodium lauryl sulphate (micelles) increases the conversion efficiency, i.e. 1.20%. The used NaLS solubilises the dye more easily and stabilizes the system and may increase the probability of charge transfer between surfactant and the dye in the system.

5. 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 learn more about the electroactive species. The possible combinations of electroactive species in photogalvanic cell are tabulated in table 7.

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.

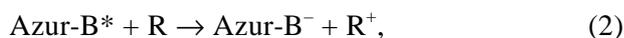
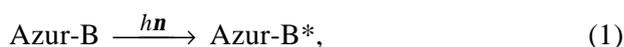
As a consequence, the maximum photocurrent (i_{\max}) and rate of increase in photocurrent should decrease with an increase in diffusion length, but this was not observed experimentally. The value (i_{eq}) is also observed to be independent with respect to change in diffusion length (rather it decrease slightly). Therefore, it may be concluded that the main electroactive species are the leuco or semi-azur-B and the dye azur-B in the illuminated and dark chambers respectively. However, the reductant and its oxidized products act only as electron carriers in the path.

6. 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



At electrode

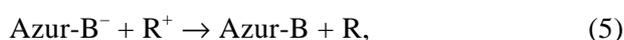


Dark chamber

At electrode



Bulk solution



where azur-B, azur-B⁻, R and R⁺ are semi or leuco forms, EDTA and its oxidized form respectively.

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