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Role of Reductants, Photosensitizers and Surfactants for Solar Energy Conversion and Storage: EDTA-Azure-A-NaLS System

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Efforts have been made to prepare some efficient photoglavanic cells using anionic micelles—sodium lauryl sulphate (NaLS), ethylene diamine tetraacetic acid disodium salt (EDTA) as an electron donor and a dye Azure-A as photosensitizer. The photogalvanic cell so prepared shows ramarkable electrical output—photopotential 814.0 mV, photocurrent 255.0 μA and power of the cell 207.57 μW. The determined conversion efficiency was 1.20% and fill factor was 0.45 where the maximum possible value is 1.0. The current-voltage characteristics have been studied in detail and a tentative mechanism for the photogeneration of current is also proposed.

Key Words: Conversion efficiency, Power point of the cell, Fill factor, Sodium lauryl sulphate, Azure-A, Ethylene diamine tetraacetic acid disodium salt.

INTRODUCTION

The direct conversion of solar energy into electricity offers the future prospects of a nonpolluting, inexhaustive, most abundantly available promising and clean source of energy with no disposal problem. Researchers in leading laboratories have well attended the conversion of solar energy and store it through photovoltaic cells, photoelectrochemical cells, photogalvanic cells, etc. The photogalvanic effect was first reported by Rideal and Williams[1], but it was systematically investigated by Rabinowitch[2,3]. Later on it was further investigated by many workers[4–11].

Theoretical conversion efficiency of photogalvanic cell is about 18% but the observed conversion efficiencies are quite low due to lower stability of dyes, back-electron transfer, aggregation of dye molecules around electrode, etc. Hoffmann and Lichtin have discussed various problems encountered in the development of the field. A detailed literature survey reveals that different photosensitizers and reductants have been used and store it. In order to increase the conversion efficiency and storage capacity of these photogalvanic cells the anionic micellar species—sodium lauryl sulphate is added and efforts were made to lower down its cost for commercial viability.

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EXPERIMENTAL

An H-shaped glass tube was fabricated and blackened keeping a window in one arm. Double distilled solutions of the dye Azure-A (Loba), EDTA (Qualigens), NaLS (SRL) and NaOH (S.D. Fine) were used in the present work. A platinum electrode (1.0×1.0 cm^2) was dipped into a limb having window and a saturated calomel electrode (SCE) was immersed into the other limb as a reference electrode and connected with digital pH-meter (Agronic model 511) and microammeter (Osaw, India) through a key and resistance to keep the circuit close and open devices and ultimately be magnified with solar radiations. The i-V characteristics of the cell were studied using an external load (log 470k) in the circuit to get a complete picture of conversion of chemical energy into electrical energy. Different wattage bulbs (ECE) were used as source of illumination.

RESULTS AND DISCUSSION

Effect of Variation of [EDTA]

With increase in concentration of the reductant [EDTA], the photopotential was found to increase till it reached a maximum. On further increase in concentration of EDTA a decrease in electrical output of the cell was observed.

The possible causes for decrease in electrical output on higher concentrations of reductant are fewer number of molecules available for electron donation in lower concentration and larger number of molecules at higher concentration, which hinder the movement of dye molecules towards electrodes, respectively. The obtained results are summarized in Table-1.

TABLE-1
EFFECT OF VARIATION OF [EDTA]

[Azure-A] = 4.92×10^{-5} M
pH = 12.78
[NaLS] = 6.4×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

EDTA-Azure-A-NaLS system	EDTA $\times 10^3$ M				
	2.32	2.28	2.24	2.20	2.16
Photopotential (mV)	155.0	593.0	814.0	307.0	198.0
Photocurrent (μA)	75.0	50.0	260.0	27.0	50.0
Power (μW)	11.62	29.65	211.64	8.28	9.9

Effect of variation of [Azure-A]

It was found that a maximum electrical output was obtained at 4.92×10^{-5} M concentrations of dye molecules.

The higher concentration of dye resulted into a decrease in electrical output as the intensity of light reaching the dye molecule near the electrode decreases due to absorption of the light by dye molecules present in the path and the decrease in electrical output at lower concentration because the fewer number of

molecules are insufficient to proceed the reaction smoothly. The results are given in Table-2.

TABLE-2
EFFECT OF VARIATION OF [AZURE-A]

[NaLS] = 6.4×10^{-3} M
pH = 12.78

[EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

EDTA-Azure-A-NaLS system	Azure-A × 10^5 M				
	5.04	4.96	4.92	4.88	4.84
Photopotential (mV)	317.0	728.0	814.0	593.0	397.0
Photocurrent (μA)	30.0	250.0	260.0	50.0	25.0
Power (μW)	9.51	182.0	211.64	29.65	9.925

Effect of variation of surfactant [NaLS]

The effect of variation of anionic micelle concentration was investigated in EDTA-Azure-A-NaLS system. It was observed that electrical output of the cell was found to increase on increasing the concentration of micelles reaching a maxima value. On further increase in their concentration, a fall in photopotential, photocurrent and power of the photogalvanic cell was observed. The possible reason for lowering in electrical output on higher and lower concentration of surfactant is due to its most active form around its critical micelle concentration. The obtained results are given in Table-3.

TABLE-3
EFFECT OF VARIATION OF ANIONIC MICELLE [NaLS]

[AzurA] = 4.92×10^{-5} M
pH = 12.78

[EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

EDTA-Azure-A-NaLS system	NaLS × 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 (μA)	150.0	160.0	260.0	50.0	80.0
Power (μW)	112.95	126.72	211.64	29.65	37.60

Effect of variation of pH

It was observed that the photogalvanic cell containing EDTA-Azure-A-NaLS is very sensitive to pH values and a maxima for electrical output at pH = 12.78 was obtained whereas there was decrease at lower and higher pH values. The obtained observations are summarized in Table-4.

TABLE-4
EFFECT OF VARIATION OF pH

[Azure-A] = 4.92×10^{-5} M
[NaLS] = 6.4×10^{-3} M
[EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

EDTA-Azure-A-NaLS system	pH				
	12.83	12.80	12.78	12.74	12.71
Photopotential (mV)	593.0	884.0	814.0	337.0	301.0
Photocurrent (μA)	50.0	150.0	260.0	50.0	70.0
Power (μW)	29.65	132.60	211.64	16.85	21.07

Effect of diffusion path length

The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell (i_{max}, i_{eq} and rate of initial generation of photocurrent) was studied using H-cells of different dimensions,

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 photocurrent behaviour is an initial rapid reaction followed by a slow rate determining step at a later stage. The results are summarized in Table-5.

TABLE-5
EFFECT OF VARIATION OF ANIONIC MICELLE [NaLS] CONCENTRATION

[Azure-A] = 4.92×10^{-5} M
[NaLS] = 6.4×10^{-3} M
pH = 12.78
[EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

Diffusion path length D_L (mm)	Maximum photocurrent i_{max} (μA)	Equilibrium photocurrent i_{eq} (μA)	Rate of initial generation of current (μA min^{-1})
35.0	298.0	274.0	20.1
40.0	298.0	274.0	20.7
45.0	300.0	275.0	23.4
50.0	302.0	276.0	25.0
55.0	303.0	277.0	26.4

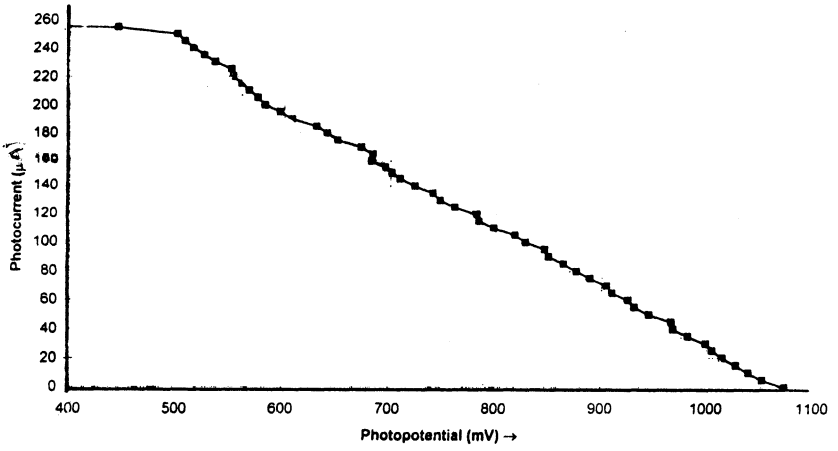
Current voltage (i-V) characteristics of the cell

The short circuit (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells were measured with a microammeter (circuit closed) and with a digital pH-meter (circuit open), respectively. The current and potential values between these two extreme values (V_{oc}) and short circuit (i_{sc}) were recorded with a carbon pot (log 470k) connected to a microammeter through which an external load was applied.

It was observed (Graph 1) that i-V curve deviated from its ideal regular rectangular shape. A point i-V curve, called power point (pp) determined where

the product of potential and current was maximum. The values of potential are V_{pp} and i_{pp} respectivel;, with the help of i-V curve, the fill factor was determined as 0.45 using the formula:

$$\text{fill factor } (\eta) = \frac{i_{pp} \times v_{pp}}{i_{sc} \times v_{oc}}$$



Graph 1. Current-voltage (i-V) characteristics of the cell

On the basis of optimum conditions the system was directly exposed to sunlight and conversion data are summarized, compared to the results when cell contained no micelles, in Table-6.

Conversion efficiency

With the help of current and potential values at power point and the incident power of radiations the conversion efficiency of the cell was determined as 1.20% by using the formula:

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

Sunlight conversion data with surfactant and without surfactant are given in Table-7.

Performance of the cell

The performance of the cell was studied by applying the external load necessary to have the current and potential at the power point after removing the source of light. It was observed that the cell can be used in the dark at its power point for 26 min whereas in absence of surfactant the cell can be used only for 11 min.

Electoactive species

On illumination there was a rapid fall in potential and after some time a constant value was obtained (on removing the source of light); the change in

potential was reversed but it never reached the initial value. It suggests that the main reversible photochemical reaction is also accompanied by irreversible side reaction. Electroactive species are the leuco dyes and dyes themselves at the illuminated and dark electrodes, respectively.

TABLE-6
CURRENT-VOLTAGE (i-V) CHARACTERISTICS OF THE CELL

[Azure-A] = 4.92×10^{-5} M
[NaLS] = 6.4×10^{-3} M
pH = 12.78
[EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2}
Temperature = 303 K

Potential (mV)	Photocurrent (μA)	Fill factor (η)	Potential (mV)	Photocurrent (μA)	Fill factor (η)
1074	0		740	135	
1053	5		723	140	
1040	10		709	145	
1028	15		701	150	
1015	20		695	155	
1005	25		682	160	
999	30		683	165	
982	35		672	170	
968	40		650	175	
966	45		640	180	
945	50		630	185	
931	55		607	190	
925	60		596	195	
910	65		582	200	
905	70		575	205	
889	75		567	210	
876	80		560	215	
864	85		552	220	
850	90		550	225	
846	95		535	230	
828	100		525	235	
818	105		515	240	
798	110		507	245	
784	115		500	250	0.59
782	120		445	255	
761	125		0	260	
747	130				

According to the observed results the most probable rate determining process for (i_{eq}) should be the recycling reaction of oxidation product (of the reducing agent) and the semi or leuco dye (photosensitizer), some experimental evidences

have been obtained by Wildes and Lichtin[26] and Yart Remy *et al.*[25] in favour of participatio of leuco form of the dyes as electroactive species.

TABLE-7
SUNLIGHT CONVERSION DATA

Surfactant [NaLS]	Conversion efficiency (%)	Photopotential (mV)	Photocurrent (μA)
Present	1.2	1560.0	335
Absent	0.32	755.0	110

On the basis of these observation a mechanism is suggested for the generation of photocurrent in the photogalvanic cell. Various possible combinations of electroactive species are summarized in Table-8.

TABLE-8
POSSIBLE COMBINATIONS OF ELECTROACTIVE SPECIES

In illuminated chamber	In Dark Chamber
AA	Oxidized form of reducant (R^+)
Leuco or semi-leuco (AA)	Oxidized form of reducant (R^+)
Leuco or semi-leuco (AA)	Oxidized form of reducant (R^+)

Mechanism

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

Illuminated chamber

$$AA \xrightarrow{h\nu} AA^*$$

$$AA^* + R \longrightarrow AA^- \text{ (semi or leuco)} + R^+$$

At platinum electrode

$$AA^- \longrightarrow AA + e^-$$

Dark chamber

$$AA + e^- \longrightarrow AA^- \text{ (semi or leuco)}$$

$$AA^- + R^+ \longrightarrow AA + R$$

where AA, AA^-, R and R^+ are Azure-A, leuco or semi-leuco forms of Azure-A, reductant and oxidized form of reductant (EDTA), respectively.

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