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Photogalvanic solar energy conversion: Study with photosensitizers Toluidine Blue and Malachite Green in presence of NaLS

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1. Introduction

In 1839, Becquerel [1] first observed the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was firstly observed by Rideal and Williams [2], later systematically investigated by Rabinowitch [3,4] in Fe(II)-Thionine system. Sakata et al. [5], Clark [6], Wildes et al. [7] and Anisworth [8] also studied this effect and discussed various problems encountered in the development of the photogalvanic cell. Dual et al. [9] observed an interesting alternating current-photogalvanic cell and De Bery and Vichbeck [10] observed the photogalvanic effect with Prussian blue modified TiO₂ electrode. Haffman and Lichtin [11], Dung and Kozak [12] and Bhowmik et al. [13] have discussed the various aspects of photogalvanic effect. Photogalvanic cell composed with different dye-reductant couple like Proflavin-ascorbic acid [14], Thionine-EDTA [15], Methylene blue-Fe(II) [16], Toluidine Blue-NTA [17], Riboflavin-EDTA [18], Rosebengal-EDTA [19], Fuschsine basic-EDTA [20], Fluoroscein-EDTA [21], Eosin-Glucose [22], have been studied with considerable photogalvanic output. Rohtagi-Mukherjee [23], Srivastava et al. [24], Bhowmik et al. [25], Jana [26] and

ABSTRACT

The photogalvanic effect of photosensitizer – reductant pair, Toluidine Blue–Arabinose and Malachite Green–Arabinose have been studied in presence of anionic surfactant NaLS (sodium lauryl sulphate) and a tentative mechanism has been proposed for the cell reaction. The photopotential (ΔV) and photocurrent (i_{sc}) were obtained 813.0 mV and 60.0 μ A in Toluidine Blue system and 348.0 mV and 36.0 μ A in Malachite Green system. The conversion efficiency and storage capacity of the developed cells were found to be 0.1448% and 123.0 min, respectively with Toluidine Blue system and 0.0590% and 32.0 min, respectively with Malachite Green system.

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Ghosh and Bhattacharya [27,28] have used different photosensitizers and reductant in photogalvanic cells.

Development of photogalvanic cells consisting of tris-(bipyridine) Ruthenium(II) complex as photosensitizer and Prussian blue as mediator was reported by Hidenobu Shiroish et al. [29].

Recently, Gangotri et al. [30–32] have reported some new photogalvanic cell systems with reasonable electrical output.

From the literature, various photosensitizers and reductants have been used with surfactants but no attention has been paid to the use of Toluidine Blue–Arabinose and Malachite Green–Arabinose system in presence of anionic surfactant sodium lauryl sulphate(NaLS). The present work studies the photogalvanic response in presence of surfactants (NaLS) in Toluidine Blue –Arabinose and Malachite Green–Arabinose system.

2. Experimental

2.1. Reagents and apparatus

The dye Toluidine Blue and Malachite Green, reductant Arabinose, surfactant sodium lauryl sulphate and sodium hydroxide were LOBA, BDH, S.D. fine and Qualigen products, respectively. All solutions of used chemicals were prepared in double distilled water.

Other necessary requirements of our experiment were a blackened H-shaped container, a platinum foil electrode of 1 cm² area, a saturated calomel electrode (SCE), a digital pH meter (Systronics model 335), a microammeter (MO-65), 200 W tungsten lamp, a



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variable resistance (log 470 K) and a UV–Visible spectrophotometer(Chemito's UV–Vis. 2600).

2.2. Procedure

- (i) Stock solution of dye (1×10^{-3} M), reductant (1×10^{-2} M), surfactant (1×10^{-1} M) and NaOH (1 N) were prepared in double distilled water. During preparation of dye solution the precaution taken was to protect the solution from light and to store in darkened container.
- (ii) Absorbance of dye solution measured with the help of UV– Visible spectrophotometer. A solution with higher absorbance was used in reactive cell solution.
- (iii) The mixture of dye, reductant, surfactant and NaOH was made up to 25.0 ml and placed in the blackened H-shaped container. A platinum foil electrode (1 cm²) immersed in one limb of cell container which contains a transparent window and a SCE was in another one. The experimental set-up is shown in Fig. 1.
- (iv) When prepared cell obtained stable dark potential value, platinum foil electrode was exposed to light. A water filter was used between light source and cell to cut-off thermal radiation. With the help of pH meter and microammeter, cell's electrical output – potential and current were measured, respectively. A load resistance was used to apply desired load in microammeter circuit to establish currentvoltage characteristics of the cell. The experimental temperature was maintained at 303 K.

3. Results

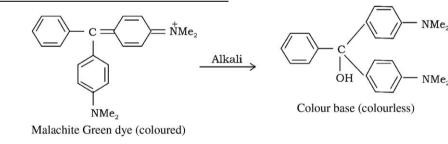
The representative data for the studied systems Toluidine Blue–Arabinose–NaLS and Malachite Green–Arabinose–NaLS are given in Table 1 which shows the over all outcome of the present studies. Blue] = 2×10^{-5} M and [Malachite Green] = 2.4×10^{-5} M. On increase or decrease in these values, cell's output decreased in both situations (Table 2).

As dye solution in the photogalvanic cell absorbs the light radiation and initiates the cell reaction, its concentration must effects the cell output and this was observed in experimental results. In presence of higher concentration of dye, density of dye molecules in path of platinum electrode should be large and therefore they absorbs major portion of light. Hence the dye molecules around the electrode will not obtain the desired light intensity and cell output gets affected. In presence of lower concentration of dye, there should be low availability of dye molecules to excite and donate electrons to the platinum foil electrode.

3.3. Effect of variation of sodium lauryl sulphate concentration

Both the systems studied with variation of surfactant concentration. The cell output increased with increased in [NaLS] but after a particular concentration, output of cell was start decrease. It was observed that with Toluidine Blue systems electrical output obtained maximum at particular concentration of NaLS = 5.6×10^{-3} . The photogalvanic response obtained maximum at 6.4×10^{-3} concentration of surfactant in Malachite Green system. Both the systems were also studied in absence of NaLS and it was observed that in the absence of surfactant, electrical output decreased. It indicates the presence of the charge transfer interaction between the dye-surfactant. The photoejection of electron from dye-surfactant depends on the charge on micelle.

Presence of NaLS is also found important to maintain the dyes colour. It was effectively observed in Malachite Green system that Malachite Green converted into colour base (colourless) on reaction with alkali in cell solution (in absence of NaLS). But in presence of NaLS colour remains maintained.



3.1. Absorption spectra of dye solution

Absorption spectra of reactive photogalvanic cell solutions containing dye solution was taken with the help of UV–Visible Spectrophotometer.

Absorption spectra of Toluidine Blue–NaLS and Malachite Green–NaLS are given in Figs. 4 and 5.

It is clear from absorption spectra of different dye-surfactant combinations that concentration of surfactant shows a remarkable effect on absorbance of dye solution. On the addition of anionic surfactant(NaLS) in dye solution an enhancement of absorbance peak obtained.

3.2. Effect of variation of dye concentration

Effect of variation of dye concentration on electrical output of cell in both the systems was studied and observed that systems worked with efficiency at a particular maximum [Toluidine It can be understood by the indicator equilibria [33], present in dye, in which two forms I_A (acidic) and I_B (basic) are related to each other as shown in the equilibrium (A)

$$I_{\rm A} + \rm OH^{-} \, \frac{k^{\rm f}}{k^{\rm f}} \, I_{\rm B} \tag{a}$$

The influence of NaLS on k^{f} and k^{r} have been investigated and it has been found that k^{f} and k^{r} both decrease in presence of NaLS. Micelles exerted a greater effect on the second-order rate constants, k^{f} , than on k^{r} , so equilibrium shifts to the left.

3.4. Effect of variation of pH of the systems

Photogalvanic response of the systems with Toluidine Blue and Malachite Green were obtained under the variation of pH of these systems. The photopotential and photocurrent increased with pH and reaches maximum at pH 12.90 and pH 12.77, respectively and then decreased with further increase in pH (Table 3). It was

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