Photogalvanic cells based on the photoreduction of xanthene dyes using riboflavin as a sensitizer in aqueous/micellar medium

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The photochemical reduction of fluorescein, eosin (Y) and rosebengal by disodium salt of EDTA using riboflavin (B) as a sensitizer has been studied in aqueous, neutral (triton X-100) and cationic (CTPB) micellar media. The two micelles (i.e. neutral and cationic) are found to catalyse the electron transfer from reduced riboflavin to the dye in the forward photoreaction. Oxidation of semi-reduced dye radical (DH) at the anode (Pt electrode) in a two-compartment photogalvanic (PG) cell which contains riboflavin, Na₂EDTA and dye (D) in the photoanode compartment and 1.0 M HClO₄ in the dark cathode compartment generates noticeable photocurrents. Remarkable increase in photocurrent is noticed in the micellar medium compared to that in the aqueous medium. The stability of the cell also increases in micellar medium.

The photogalvanic effect arising from photochemical redox reactions in solution has attracted the attention of many workers in recent years. Most of the previous work has been done on thionine-ferrous ion (Fe²⁺) systems. One of the major obstacles to efficient photoconversion via photogalvanic cells is the competition between energy wasting back reactions and current producing electrode processes. The other major obstacle is the low efficiency of electron transfer reactions. One way to circumvent these problems is to maintain the optimum distance between the donor and acceptor by incorporating the substrate molecules in microheterogeneous media such as microemulsions, micelles, polymer membranes or lipid layers. Nickerson et al. reported that in the photochemical reduction of tetrazolium salts in aqueous medium by disodium salt of EDTA, riboflavin acts as a sensitizer as well as a hydrogen atom carrier. This prompted us to study the reduction of xanthene dyes both in aqueous and micellar media using riboflavin as a sensitizer and Na₂EDTA as a reducing agent. Our aim was to find out whether photocurrents and photovoltages could be generated with riboflavin as sensitizer, and if it was possible to do so then to establish whether micellar medium has any positive effect on the generation of photocurrents and voltages and on the stability of the cell.

Materials and Methods
All the chemicals used were of AR grade and purified by recrystallisation wherever necessary. In all these experiments the concentration of the micelle was maintained above its critical micellar concentration (cmc).

The light source used was a Hanovia (UVS 500) medium pressure mercury vapour lamp. The intensity of the light falling on the cell was measured with a conventional potassium ferrioxalate actinometer and found to be 6.21 × 10¹⁷ quanta sec⁻¹.

The photogalvanic cell consisted of two identical parts fitted with B₁₄ sockets and a side arm. Platinum electrodes were fused to the B₁₄ cones with mercury contact. The cathode half-cell was filled with 1.0 M HClO₄ and the anode with solutions of Na₂EDTA, riboflavin, KCl (supporting electrolyte) and dye in aqueous or micellar medium. The anodic solution was deaerated by passing oxygen-free N₂ gas. The anodic reaction mixture was buffered to pH 7.0-7.4. The two half-cells were connected by means of a salt bridge inserted in the side tube. When required, stirring could be provided for both the photoanode and cathode compartments. Photocurrents and photovoltages were measured by a PG 1000 digital multimeter. The load resistance was 10³ kΩ and the internal resistance of the cell was negligible (< 10⁻⁶ kΩ).

The absorption spectra of the dye in aqueous or micellar medium were recorded on a Beckman DU-spectrophotometer.

Results
Photogalvanic cell studies
The photoreduction of the dye by Na₂EDTA
using riboflavin as a sensitizer in anaerobic conditions was carried out in the photoanode compartment of a two-compartment PG cell. The dark current stabilized in about 10 min; the dark current and voltage were found to be 10-20 µA and 15-25 mV respectively. These values depend on the photoanode reaction mixture and cannot be neglected. Exposure of the anode half-cell to light lead to immediate generation of photocurrents and photovoltages. The most important change noticed was the photo-bleaching of the dyes due to generation of semi-reduced dye radicals (DH); the initially coloured photoanode solution became colourless and remained so for several hours of irradiation. During illumination, the observed photocurrent ($I_{\text{obs}}$) and photovoltage ($V_{\text{obs}}$) increased with time and it reached constant values probably due to establishment of steady-state concentration of the semi-reduced dye radicals in the photoanode compartment. The maximum photocurrent ($I_{\text{max}}$) of the cell was calculated by subtracting $I_{\text{dark}}$ from $I_{\text{obs}}$. Similarly, the maximum photovoltage ($V_{\text{max}}$) was obtained from the difference between $V_{\text{obs}}$ and $V_{\text{dark}}$.

<table>
<thead>
<tr>
<th>Dye (D)</th>
<th>Medium</th>
<th>$I_{\text{max}}$ (µA)</th>
<th>$V_{\text{max}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triton X-100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTPB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eosin</td>
<td>Triton X-100</td>
<td>180</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>CTPB</td>
<td>240</td>
<td>540</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>Triton X-100</td>
<td>205</td>
<td>490</td>
</tr>
<tr>
<td></td>
<td>CTPB</td>
<td>390</td>
<td>595</td>
</tr>
<tr>
<td>Rosebengal</td>
<td>Triton X-100</td>
<td>240</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>CTPB</td>
<td>440</td>
<td>635</td>
</tr>
</tbody>
</table>

Photochemical reactions:

\begin{align*}
B_2 + h\nu \rightarrow & \ 3B_2 & \quad \text{(1)} \\
3B_2 + RH \rightarrow & B_2H + \tilde{R} & \quad \text{(2)} \\
\end{align*}

Dark reactions:

\begin{align*}
B_2H + \tilde{R} \rightarrow & B_2H_2 + R_{(ox)} & \quad \text{(3)} \\
B_2H + D \rightarrow & B_2 + DH & \quad \text{(4)} \\
B_2H_2 + D \rightarrow & B_2H + DH & \quad \text{(5)} \\
\tilde{B}_2H + DH \rightarrow & B_2 + B_2H_2 & \quad \text{(6)} \\
\tilde{B}_2H + DH \rightarrow & B_2H + DH_2 & \quad \text{(7)} \\
\tilde{D}H + B_2 \rightarrow & \tilde{B}_2H + D & \quad \text{(8)} \\
\tilde{D}H + \tilde{B}_2H \rightarrow & \tilde{B}_2H_2 + D & \quad \text{(9)} \\
\end{align*}

Electrochemical reactions:

Anode: $\tilde{D}H \rightarrow D + H^+$ 

Cathode: $H^+ + e^{-} \rightarrow \frac{1}{2} H_2$

where $B_2 = \text{riboflavin}; \ 3B_2 = \text{triplet riboflavin}; \ RH = \text{reducing agent (Na}_2\text{EDTA)}; \ \tilde{B}_2H = \text{semi-reduced riboflavin radical}; \ R = \text{semi-oxidized form}$

Discussion

The mechanism of photoreduction of the dye by Na$_2$EDTA using riboflavin as a sensitizer is well established$^{14,16}$ (Scheme 1):
of Na₂EDTA; B₂H₂ = reduced riboflavin, R(ox) = oxidized form of Na₂EDTA; D = dye; DH = semi-reduced dye radical; DH₂ = reduced dye; H⁺ = hydrogen cation; H₂ = hydrogen gas.

The maximum photocurrent (Iₘₘₐₓ) obtained from the PG cell was found to be proportional to the intensity of light (I). It is, therefore, concluded that, among the possible two anodic reactions, viz., DH → D + H⁺ and DH₂ → DH + H⁺, only the former is important since the concentration of semi-reduced dye [DH] is proportional to light intensity (I) and the concentration of the reduced dye [DH₂] is thought to be proportional to I². A similar explanation was given by Sakata et al.17 for Fe²⁺-thionene system. In view of this, only the former step, viz., DH → D + H⁺, is included in the above mechanism.

The maximum photocurrents (Iₘₘₐₓ) and photovoltages (Vₘₘₐₓ) are higher in micellar medium compared to those in aqueous medium (Table 1). This could probably be due to adsorption (the so-called concentration effect) of some or all the substrates, viz., dye, riboflavin, Na₂EDTA on the surface of the micelle which must be responsible for the reactions (1-5) of Scheme 1 occurring rapidly in micellar medium. Probably, the required geometry is also provided by the micelle for efficient electron transfer.

Fluorescence and absorption spectral studies of anionic rosebengal by Kapoor et al.18 revealed reduction in the intensity of λₘₘₐₓ of the rosebengal and a shift in the λₘₘₐₓ when various neutral or cationic surfactants (above their cmc) were added to rosebengal solution. This has been explained to be due to adsorption of the rosebengal on the surface of the micelle which was considered to be spherical in nature. A similar result was obtained in the present case also (Fig. 1). Kunitake et al.20 from their study on the reduction of riboflavin by thiols in micellar medium reported that riboflavin is adsorbed on the hydrophobic part of the micelle. The reducing agent Na₂EDTA, which is anionic, is expected to localize on the surface of the cationic micelle due to coulombic forces of attraction. From these observations it is clear that all the substrates, viz., dye, riboflavin and Na₂EDTA are adsorbed on the surface of the cationic micelle whereas in the case of neutral micelle only the dye and riboflavin are adsorbed on the surface of the micelle. The data in Table 1 support this contention. The maximum photocurrents (Iₘₘₐₓ) and photovoltages (Vₘₘₐₓ) obtained in different media are in the order: Aqueous < triton X-100 (neutral) < CTPB (cationic).

This trend can be explained on the basis of presence of charge on the micelle and the reactants and the number of reactants adsorbed on the surface of the micelle. Since triton X-100 is neutral, both dye (anionic) as well as riboflavin (neutral) get adsorbed on the surface of the micelle due to their hydrophobic character. While the reducing agent Na₂EDTA, which is anionic, is not adsorbed on the surface of the micelle. Therefore, the reactions (1-5) of Scheme 1 are faster in micellar medium than in aqueous medium. CTPB being cationic in nature, all the reactants, viz., sensitizer, dye, reducing agent get adsorbed and, hence, the Iₘₘₐₓ values are highest in CTPB.

From PG cell studies it is clear that the stability of the cell is high in cationic micellar medium (>36 hr) compared to that in aqueous medium (≈6 hr). This is probably due to considerable reduction in the rate of back reactions, viz.,

\[ \text{DH} + \text{B₂H} \rightarrow \text{D} + \text{B₂H₂} \]
\[ \text{DH} + \text{B₂H₂} \rightarrow \text{D} + \text{B₂H} \]

This could be due to distribution of the negative charge associated with DH radicals over the positive surface charge of the micelle thus preventing it (DH) from giving away a hydrogen atom to B₂H (ref. 8, 9). From these studies it is concluded that cationic micelle (CTPB) is the most efficient of the surfactants used for these reactions.

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References
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