Electrochromic Properties of Functional Squarylium Dyes

Sung Hoon Kim* & Seok Hwan Hwang
Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taege 702-701, Korea
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ABSTRACT

The electrochromic properties of some squarylium dye (SQ) were studied by using BuOH/CH₂Cl₂(4:6/v:v) solution with Bu₄NClO₄ as supporting electrolyte. The electrochromic display (ECD) cell of these squarylium dyes coloured blue in open-circuit condition, but changed to a green colour at 1.41 ~ 1.8 volt. At an applied voltage in the range higher than 2.1 volt, the absorbance at 480 nm and 630 nm decreases rapidly and the reversible colour change in open-circuit condition disappeared. The cyclic voltametric behaviour of the dyes was investigated and the first and second oxidation potentials measured. Decolouration rates in open-circuit were found to be first-order processes. © 1997 Elsevier Science Ltd

Keywords: electrochromism, squarylium dye, display, ITO glass, cyclic voltammetry.

INTRODUCTION

Electrochromism is a reversible colour change in a material caused by an applied electric field or current. Although inorganic systems are now in practical use, organic systems have advantages over inorganic systems in several ways, viz. operation at low voltage, coloration over a wide range, colour distinction, and multi-colouration, etc. A large number of organic compounds develop absorption bands in the visible region of the spectrum upon redox reaction and most compounds in this class exhibit electrochromic
phenomena by reversible electrode deposition, e.g. viologens [1], pyridines [2], ortho-toluidines [3], and anthraquinones [4]. The coloration is achieved by an oxidation-reduction reaction, which can be a simple redox reaction or a redox reaction coupled with a chemical reaction to produce an insoluble coloured species. We have reported that the response improved electrochromic two colour display using two kinds of viologen derivatives [5].

In this study, three kinds of squarylium dye contain an indoline ring in the molecule have been synthesized, and exhibit distinct electrochromism in a comparatively low voltage region. Squarylium dyes are 1,3-disubstituted products obtained from squaric acid and two equivalents of various types of electron donating carbo and heterocycles such as azulene [6], pyrroles [7], or heterocyclic methylene bases [8] in an azeotropic solvent. The synthesis of squarylium dyes is simple and has been reviewed several times in the literature [9–11]. Despite the relatively wide range of properties of squarylium dyes now known, no electrochromic properties concerning with the redox reaction have yet been reported.

During the course of our investigation on the synthesis and photostability of squarylium dyes containing an indoline ring [12], we have found that squarylium dyes 4a, 4b and 4c exhibit electrochromic properties in solution. Squarylium dyes exhibit intense and panchromatic absorption from the visible to the near-infrared (400–1000 nm) in the solid state. These features have made them very attractive for various technological applications in industry, e.g. electrophotographic imaging [13], organic solar cells [14], optical recording [15], etc.

EXPERIMENTAL

Melting points were determined using an Electrothermal IA 900 and are uncorrected. The visible spectra were measured using a Shimadzu U.V.-2100 spectrophotometer. Elemental analysis was recorded on a Carlo Elba Model 1106 Analyzer. Cyclic voltamograms were measured using a BAS 100B/W WON A TECH. Current density was measured with a Fluke 867 graphical multimeter.

Synthesis of squarylium dyes and intermediates

N-alkylation of 2,3,3-trimethylindolenine 1 (general method)

2,3,3-trimethylindolenine, 1, (1.2 g, 7.54 mmol) and methyl iodide (1.07 g, 7.54 mmol) were refluxed for 7h in 70ml of acetonitrile. After the reaction, 1,2,3,3-tetramethylindolendenium iodide 2a, was obtained in 67.8% yield (1.54 g) by filtration.
1-Ethyl-2,3,3-trimethyl indolenium iodide 2b, was obtained by a similar procedure using ethyl iodide.

**Preparation of squarylium dye, 4a, (general method)**
Squaric acid 3 (0.68 g, 6 mmol) and 2,3,3-trimethylindolenine 1 (1.9 g, 11.9 mmol) were heated under reflux for 3 h in a mixture of 60 ml of n-butanol/benzene (4:1/v:v) containing 3 ml of quinoline. Water was removed azeotropically using a Dean-Stark trap. The reaction mixture was cooled to room temperature. The precipitated crude products were separated by filtration and washed with n-hexane. Yields and characterisation data are shown in Table 1.

The squarylium dyes 4b and 4c were obtained by a similar procedure using 1,2,3,3-tetramethylindolenium iodide 2a, and 1-ethyl-2,3,3-trimethylindolenium iodide 2b, respectively.

**Preparation of ECD cell and electrochemistry**
The ECD cell comprised two glass sheets (3 cm x 3 cm) separated by a 0.1 mm thickness spacer of PET film. The glass sheets were coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell, and the edges of the cell were sealed with insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with a BuOH/CH₂Cl₂(4:6/v:v) solution of 0.05 mmol dye (4a, 4b, 4c) and 1.5 mmol tetrabutyl ammonium perchlorate, Bu₄NClO₄, as electrolyte. The characteristic oxidation potentials of cation and dication formation of the squarylium dyes were obtained by cyclic voltametry. All potential measurements were referred to a saturated calomel electrode (SCE). The data were obtained with degassed solvent, BuOH/CH₂Cl₂, and tetrabutyl ammonium perchlorate as electrolyte. The electrochromic solutions were deaerated with nitrogen gas. The working electrode was a glassy carbon and the counter electrode was platinum. All experiments were run at room temperature.

**RESULTS AND DISCUSSION**
Squarylium dyes are normally synthesized by condensation of squaric acid 3, and electron rich aromatic or heteroaromatic compounds. The squarylium dyes in this work were synthesized from squaric acid and 2,3,3-trimethylindoline 1, 1,2,3,3-tetramethylindolenium iodide 2a, or 1-ethyl-2,3,3-trimethylindolenium iodide 2b, according to modified literature procedures. Scheme 1 [8, 16].
Absorption spectra and analysis data are shown in Table 1. The absorption spectra of the coloured ECD cell produced on the anode after electrocolouration are shown in Fig. 1 (A). The threshold voltages for the coloration are about 1.4 V for dye 4a. In the 4a system (cell I), the prominent peak appears at 480 nm and the absorbance at 654 nm (which is the $\lambda_{\text{max}}$ of dye 4a) decreases significantly, depending on the increment of the applied voltage.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Yield (%)</th>
<th>$\lambda_{\text{max}}$(nm)</th>
<th>$\varepsilon$($\times 10^5$)</th>
<th>M.P. ($^\circ$C)</th>
<th>Analysis (%)</th>
<th>Found/Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>55</td>
<td>654</td>
<td>1.33</td>
<td>270$\sim$272</td>
<td>78.45</td>
<td>6.20</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>78.75</td>
<td>6.10</td>
</tr>
<tr>
<td>4b</td>
<td>61</td>
<td>633</td>
<td>3.21</td>
<td>&gt;300</td>
<td>79.03</td>
<td>6.86</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>79.21</td>
<td>6.64</td>
</tr>
<tr>
<td>4c</td>
<td>66</td>
<td>639</td>
<td>8.30</td>
<td>299</td>
<td>78.52</td>
<td>6.75</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>78.60</td>
<td>6.98</td>
</tr>
</tbody>
</table>

*Measured in CHCl$_3$.  

**TABLE 1**

Characterisation Data for Squarylium Dyes
The cell I coloured blue in open-circuit condition, but changed to a green colour at 1.4–1.8 volt. In this system, equilibrium between SQ° and SQ+ was observed and an isobestic point was found at 545 nm. We observed the reversibility of the phenomenon. It was found that two species, viz, one electron oxidized dye SQ+, and non-oxidized dye SQ°, existed in this condition, and that the equilibrium was influenced greatly by the strength of the applied voltage.

Figures 1(B) and (C), show the absorption spectra of oxidized 4b (cell II) and 4c (cell III), respectively, for different applied voltages. The ECD cell of all systems coloured green at 1.4–1.8 V, but changed to blue in open-circuit condition. The close similarity between the spectra of Figs 1(B) and (C) and the spectrum shown by Fig. 1(A), suggest that the SQ dyes 4a, 4b and 4c have the same electrochemical behaviour.

At an applied voltage in the range higher than 2.1 V, the absorbance at around 475 and 633 nm decreases rapidly, and the reversible colour change found in open-circuit condition disappeared (Fig. 1(B)). Voltametric analysis offers the most sensitive in-situ characterization of redox species. Figure 2 shows the cyclic voltamogram of dyes 4a, 4b and 4c. The anodic scan exhibits two successive oxidation waves at 0.64 V and 0.91 V versus SCE for 4b and 4c, and two cathodic peaks are shown in the backward scan. In comparison with 4b and 4c, 4a shows a shift of both the first and second oxidation potential, 0.71 V and 1.27 V, to a more positive value. This implies that dyes 4b and 4c oxidize more easily than 4a.

It has been accepted that the peak near 0.64–0.71 V corresponds to the first oxidation-reaction eqn (1) of SQ°. The peak near 0.91–1.27 V is generally considered to be the oxidation of SQ+ as shown in eqn (2).

\[
SQ^0 - e^- = SQ^+ 
\]

\[
SQ^+ - e^- = SQ^{2+} 
\]  

We propose that the reversible colour change from blue to green at 1.4–1.8 V corresponds to the first oxidation and second oxidation of SQ+, which occurred at 2.1 V in the ECD cell.

Figure 3 shows the resultant optical and current response of dyes 4a, 4b and 4c at an applied voltage of 1.8 V. As can be seen in Fig. 3, all of the ECD cell shows absorbance change within 30 s. Response times and current densities are about same when 1.8 volt is switched in the ECD cell. Thus, the electrochemically grown SQ dyes 4a, 4b and 4c are good candidates for electrochromic displays.
Fig. 1. Absorption spectra of the ECD cell depending on the applied voltage 1.4 \sim 1.8 \text{ V.} (A) cell I (B) cell II (C) cell III.
Response times are very short and are acceptable, but lifetime is a problem and does not compete with the lifetime obtained with inorganic electrochromic materials such as tungsten oxide (10^6 cycles).

The rate of the green to blue colour change in open-circuit condition was also examined. Tomioka has examined the thermal decolouration rate for photochromic spiropyran derivatives using first-order kinetics [17]. The kinetic equation approach to the green to blue colour change via first-order reaction, $SQ^+ \rightarrow SQ^0$, i.e. in the present case, is given by

\[ A_t - A_\infty = A_i \cdot \exp(-kt) \]  \hspace{1cm} (3)

where $A_0$ is the absorbance near 480 nm under 1.8 V, and $A_t$ is the absorbance near 480 nm at any time $t$ after open-circuit. $A_\infty$ and $k$ refer to absorbance near 480 nm after 48 h and first-order colour changing rate constant, respectively. In the colour changing process, the kinetic analysis predicts the logarithm of the difference between $A_\infty$ and $A_t$ at time $t$ to be linear with time, the slope giving the decolouration rate constant, $k$. First order plots
Fig. 3. Applied cell voltage and resultant optical and current response of SQ(4a), SQ(4b) and SQ(4c).
Fig. 4. Plot of $-\ln(A_t - A_\infty)$ as a function of time according to eqn (3) for the colour change reaction of SQ4a ($\bullet$), SQ4b ($\blacksquare$) and SQ4c ($\triangle$) according to eqn (3) for 4a, 4b and 4c in ECD cell are shown in Fig. 4. The profile was almost the same in cell I, cell II, and cell III, and the colour change rate constants $k_{4a} = 33.6 \times 10^{-2}$ s$^{-1}$, $k_{4b} = 38.2 \times 10^{-2}$ s$^{-1}$, $k_{4c} = 28.1 \times 10^{-2}$ s$^{-1}$ were obtained from the slope.

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REFERENCES