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The reduction mechanism of *p*-cyanophenylviologen in PVA-borax gel polyelectrolyte-based bicolor electrochromic devices

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ABSTRACT

Polyelectrolyte-based electrochromic devices containing *p*-cyanophenylviologen and PVA-borax gel provide two different well-defined colored states (green and red). In this work, the bicolor electrochromic gel was characterized by *in situ* electron spin resonance (ESR)/ultraviolet–visible–near infrared (UV–vis–NIR) spectroelectrochemistry to get more information about the electron transfer reactions of the *p*-cyanophenylviologen dication (p-CV^{2+}) in the PVA-borax gel medium. We have determined the dominant species at each stepwise varying potential and proposed the complete mechanism of the p-CV^{2+} reduction in polyelectrolyte. The species responsible for the green and red coloration were identified. The switching between bleached and colored states over repeated cycles was performed for the electrochromic devices to evaluate the redox stability of the colored species. In addition, the gel formulations were optimized in terms of optical contrast.

1. Introduction

The viologens (1,1′-disubstituted 4,4′-bipyridinium salts) are very well studied compounds used in a variety of fields such as electrochromic devices (ECDs), herbicides, solar energy conversion and molecular electronics [1]. The three common redox forms of viologens are a) the dication, b) the radical cation obtained by one-electron reduction of the dication, and c) the di-reduced (neutral) form observed after one-electron reduction of the radical cation or two-electron reduction of the dicationic form. ECDs based on viologens benefit from the mainly colorless dicationic and deeply colored radical-cationic viologen forms, whereas the di-reduced species are not usually considered due to their lower stability.

The color displayed by the radical-cationic forms depends on the nature of the substituents at the nitrogen atoms. The compounds with alkyl substituents show blue/violet coloration, whereas green color is usually observed, when both substituents are in conjugation with the bipyridine core (e.g. aryl groups). In the case of the 1,1′-bis(*p*-cyanophenyl)-4,4′-bipyridilium salts (*p*-cyanophenylviologen, *p*-CV), the colorless dication p-CV^{2+} and the green radical cation p-CV$^{\bullet+}$ have been widely studied [2–4]. The little number of works have reported on the neutral form p-CV^0 and its scarlet-red coloration, since it is highly unstable due to its powerful reducing properties [1]. The stabilization of the di-reduced species opens the possibility to extend the electrochromic color palette [5].

In Scheme 1 five common reactions of the *p*-CV are shown. Viologen radical cations can be produced by chemical [6,7] or electrochemical [8] reduction as well as by photolysis [9] of viologen dications (1).

$$p\text{-}\mathrm{CV}^{2+}\xrightarrow{+e^-}p\text{-}\mathrm{CV}^{\bullet+} \qquad (1)$$

$$2\,p\text{-}\mathrm{CV}^{+\bullet}\leftrightarrow(p\text{-}\mathrm{CV}^{\bullet+})_2 \qquad (2)$$

$$p\text{-}\mathrm{CV}^{\bullet+}\xrightarrow{+e^-}p\text{-}\mathrm{CV}^{0} \qquad (3)$$

$$p\text{-}\mathrm{CV}^{0}+p\text{-}\mathrm{CV}^{2+}\leftrightarrow\;2\,p\text{-}CV^{\bullet+} \qquad (4)$$

$$(p\text{-}\mathrm{CV}^{\bullet+})_2\leftrightarrow(p\text{-}\mathrm{CV}^{0})_2 \qquad (5)$$

Scheme 1. Common reactions of the *p*-CV.

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While in some solvents such as propylene carbonate the three redox forms of *p*-CV are soluble, in aqueous solution the *p*-CV radical cation salt and the di-reduced (neutral) form are insoluble [3,10], and the latter also exhibit limited electrochemical reversibility [11,12].

A monomer-dimer equilibrium (2) was proposed by *Schwarz* [13]. *Kosower* et al. suggested that the dimer (p-$CV^{\bullet+})_2$ is a face-to-face complex of two radical cations interacting through their π-orbitals [14]. The monomer-dimer equilibrium is observed in water at room temperature, while in polar organic solvents such as acetonitrile, propylene carbonate, dimethylformamide, etc., no dimer is formed, because ion pair formation precludes dimerization. The dimer of the viologen radicals are characterized by absorption bands which are slightly blue-shifted with respect to the radical cation ones [15].

One-electron reduction of the radical cation leads to the formation of the di-reduced (neutral) viologen (3). The viologens undergo a comproportionation reaction in which one mole of dications reacts with one mole of di-reduced species to form two moles of radical cations (4). The comproportionation has been demonstrated for the *p*-cyanophenylviologen in propylene carbonate [15,16] and in water solutions [3] by the electron spin resonance (ESR) technique, which allows detecting paramagnetic species such as the p-$CV^{\bullet+}$, while it displays no signal when only diamagnetic species such as the p-CV^0 are present in the system. Further studies of the solution phase and solid-plus-solution phase *p*-CV system with *in situ* ESR spectroscopy, UV–vis spectroelectrochemistry, diffuse-reflectance voltammetry and rotating ring-disc electrode measurements concluded that the comproportionation clearly occurs in solution, between solution and solid and very likely between p-CV^{2+} and p-CV^0 both in the solid state [17]. Here the formation of (p-$CV^0)_2$ pairs (5) was also proposed. Due to the comproportionation reaction, which is favored by the strong reducing properties of the p-CV^0, the red color of the di-reduced form cannot be generally observed, unless some strategies are implemented to stabilize the neutral form, such as inclusion of the viologen within a cyclodextrin cavity or polymer matrix [1].

We have recently shown that the transmission-mode devices based on p-CV^{2+} and poly(vinyl alcohol) (PVA)-borax gel as polyelectrolyte provide a colorless off state and two different well-defined colored states [18]. In this system the application of the less negative potential leads to the observation of the green coloration, while the more negative applied potential generates the red one. In the case of a reference aqueous liquid system, the red coloration was not detected as also reported by other groups [11,12]. The high viscosity of the polyelectrolyte gel hinders an encounter between the dications and di-reduced species and thus prevents a comproportionation reaction. That reveals that the PVA-borax gel polyelectrolyte could stabilize di-reduced species making possible the observation of not only the green but also red coloration. Although a previous spectroelectrochemical study based on three-electrode ECD architecture suggested a correlation of green and red coloration with the first and second reduction processes of viologen, further confirmation of the formed redox species (in particular, dimer structures) through more accurate techniques would be of particular interest as already stated [5].

In this work we provide new insight into the electron transfer mechanism in the polyelectrolyte-based electrochromic system. The *p*-cyanophenylviologen in PVA-borax gel polyelectrolyte has been investigated by *in situ* ESR/UV–vis–NIR spectroelectrochemistry in order to elucidate which species are involved in the different colored states. Only *in situ* spectroscopic techniques give the possibility to identify the species formed in sequence during electrochemical doping [19–21]. In addition, the switching between bleached and colored states over repeated cycles was performed for ECDs to evaluate the redox stability of the colored species, especially the di-reduced ones.

2. Experimental

2.1. Materials

Sodium tetraborate decahydrate (borax, 99.5%), poly(vinyl alcohol) (PVA, Mw 61 000), potassium ferricyanide (99%), potassium ferrocyanide (98.5%) and dimethyl sulfoxide-d6 (DMSO-d_6) were purchased from Sigma-Aldrich and used without further purification. Fluorine-doped tin oxide (FTO)-coated glass substrates (surface resistivity 6–8 Ω sq^{-1}) were provided by Solems and cleaned with warm acetone prior to use whereas UV-curing adhesive (NOA) was purchased from Norland Products Inc. Indium doped tin oxide (ITO) coated glass substrates (Merck, surface resistivity 30 Ω sq^{-1}) were used for spectroelectrochemical measurements.

2.2. Synthesis of p-CV

1,1′-Bis(*p*-cyanophenyl)-4,4′-bipyridilium dichloride (*p*-cyanophenylviologen dichloride, *p*-CV) was synthesized following a previously reported procedure [1] with minor modifications [18].

^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.77 and 9.18 ppm (d of d, 4H $J = 4.00$ Hz and 4H $J = 3.84$ Hz, Ar H), 8.35 and 8.23 ppm (d of d, 4H $J = 7.56$ Hz and 4H $J = 7.26$ Hz, bipyridine); IR (bulk ATR): ν (cm^{-1}) = 3091 (C–H olefin st), 2227 (–CN st), 1629(C=N st), 1603, 1508 (C=C st), 831 (*o*-phenylene H); IC: % Cl^- calculated for $C_{24}H_{16}N_4Cl_2$: 16.4%, found 15.0%.

2.3. Preparation of PVA-Borax electrochromic gels

General procedure: Electrochromic (EC) gels were obtained following a previously reported procedure [22]. The required amount of electroactive components (potassium ferrocyanide/ferricyanide redox pair and p-CV^{2+}) were added to a 4% aqueous solution of PVA followed by stirring. The homogeneous solutions obtained were mixed with a 4% borax aqueous solution in a 4:1 volumetric ratio and stirred with a spatula. The resulting formulations were left standing prior to use to achieve completely bubble-free gels.

Preparation of p-CV gel 1 and p-CV gel 2: The electrochromic gels were prepared keeping the concentration of potassium ferrocyanide/ferricyanide redox pair at 4 and 0.5 mmol L^{-1} values, respectively, while the concentration of p-CV^{2+} was fixed at 3.5 mmol L^{-1} in both cases.

Preparation of EC gels with varying concentration of p-CV^{2+} *viologen:* A series of nine electrochromic gels was prepared with a fixed concentration of potassium ferrocyanide/ferricyanide redox pair as an electron mediator (0.4 mmol L^{-1}) and varying concentration of p-CV^{2+} from 0.25 to 4.0 mmol L^{-1} (0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mmol L^{-1}).

2.4. Fabrication of two-electrode (2-E) electrochromic devices

2-E ECDs were assembled according to previously reported procedure [22]. Briefly, the EC gel was spread on the conducting side of the substrate provided with a spacer (220 μm thick and 2 mm wide double-side adhesive tape frame) and covered with the other electrode substrate by applying a slight pressure. Once the EC gel adapted to the shape of the electrodes, both electrodes were connected to the potentiostat using crocodile clips.