

Electrochemical Properties of Charge Transfer Complexes of 4,4'-bipyridine with Benzoquinone Derivatives

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Abstract: The electrochemical characteristics of charge transfer complex of 4,4'-bipyridine with benzoquinone derivative have been investigated using cyclic voltammetry, convolutive voltammetry and digital simulation methods. Cyclic voltammetry experiments were performed at a platinum working electrode. The electrode reaction pathway, the relevant chemical and electrochemical parameters of the investigated complex were determined using cyclic voltammetry, convolution - deconvolution transforms. The extracted electrochemical parameters and the nature of the electrode reaction were verified & confirmed via digital simulation method.

Keywords: Cyclic voltammetry, Convolutive voltammetry, Bipyridine, Digital simulation.

1. INTRODUCTION

Bipyridine complexes absorb intensely in the visible part of the spectrum. The electronic transitions are attributed to metal-to-ligand charge transfer (MLCT). In the "tris (bipy) complexes" three bipyridine molecules coordinate to a metal ion, written as $[M(\text{bipy})_3]^{n+}$ (M = metal ion; Cr, Fe, Co, Ru, Rh and so on; bipy = 2,2'-bipyridine). These complexes have six-coordinated, octahedral structures and two enantiomers. These and other homoleptic tris-2,2'-bipy complexes of many transition metals are electroactive. Often, both the metal centred and ligand centered electrochemical reactions are reversible one-electron reactions that can be observed by cyclic voltammetry. Under strongly reducing conditions, most tris(bipy) complexes can be reduced to neutral derivatives containing bipy ligands. Examples include $M(\text{bipy})_3$, where M = Al, Cr, Si [1-3].

Tris(2,2'-bipyridine) ruthenium(II) complex ($[\text{Ru}(\text{bpy})_3]^{2+}$) has been one of the most extensively studied and widely used in the field of photocatalysis, electrocatalysis and photoelectrochemical cells [4-6]. The unique combination of chemical stability, redox properties and excited state reactivity has attracted much attention

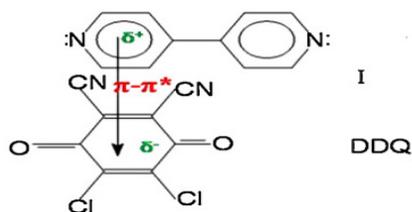
of many research groups.

However, so far the studies on this complex are limited only in solution and at chemically modified electrodes [5-7]. The electrochemical reactions of ruthenium (II)/polypyridyl complexes have been the subject of numerous investigations. Especially useful have been the Ru(II)/Ru(III) redox potentials that can be used to correlate the energy difference between the HOMO and the LUMO orbitals with the spectroscopic data [8]. Correlations have also been found between the charge transfer (CT) energies and Ru(II)/Ru(III) potentials [9 - 14]. These correlations have been used in the design of new ruthenium/bipyridine complexes with desired spectroscopic, electrochemical, and CT properties [15, 16]. An effective method of varying these properties is to modify the bipyridine ligand by adding the electron withdrawing or electron donating substituents in different positions [17, 18].

4,4'-Bipyridine belong to an important class of compounds with wide applications in different fields and since the formation charge transfer compounds give opportunity to improve the physical and chemical properties of different donors so charge transfer compounds of 4,4'-bipyridine (Bpy) with 2,3-dichloro-5,6-dicyano-1,4'-benzoquinone (DDQ), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone [chloranilic acid] (CHA) and 2,3,5,6-tetrachloro-

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Scheme 1. The molecular structure of charge transfer transition of Bpy-DDQ,



1,4'-benzoquinone [chloranil] (CHL) were studied.

Bipyridine is an aromatic heterocyclic compound representing a very important class of compounds which possess a system of π and n -electrons. Paraquat (1,1'-dimethyl - 4,4'-bipyridinium ion), also known as methyl viologen gave many applications such as electron transfer inhibitor, a redox indicator in analytical systems and monomers in polymer formation [19, 20].

Charge transfer complexes of 2,2'-bipyridine with picric acid and chloranilic acid was studied. The IR and ^1H NMR spectroscopic data indicate a charge transfer interaction associated with a proton migration from acceptor to donor followed by intramolecular hydrogen bonding [21]. Molecular complexes of paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) and chloranil with phenylhydrazones studied spectrophotometrically, and CT spectra, thermodynamic parameters and stability constants of the complexes was reported [22].

To the best of our knowledge, there is no report on the electrochemical properties of charge transfer complex of 4,4'-bipyridine with benzo-quinone derivative. So the present study is aimed to investigate the electrochemical behaviour of CT complex of 4,4'-bipyridine with benzoquinone derivative at platinum electrode in nonaqueous media. Also in this paper, the electrochemical parameters of the investigated compound are determined via cyclic voltammetry, convolutive voltammetry and digital simulation techniques.

2. EXPERIMENTAL

2.1. Materials

4,4'-Bipyridine was purchased from Aldrich Chemical Co., and it was used without further purification. DDQ was used as bought from Aldrich Co. All solvents used were of spectral pure grade (BDH or Merck).

2.2. Synthesis of the solid CT complexes

1:1 solid CT complex of 4,4'-bipyridine with the acceptor used was prepared by mixing ethanolic solution of 4,4'-bipyridine (3.0 mmol) with DDQ (3.0 mmol). The CT complex formed immediately. The separated CT solid complex was filtered and washed several times with minimum amounts of ethanol and then dried.

2.3. Electrochemical measurements

Cyclic voltammetry and convolution-deconvolution transforms were performed using a Princeton Applied Research (PAR) Computer-controlled Potentiostat Model 283 and PAR Model 175 Universal Programmer (from EG and G). The system allowed the use of any scan up to 100 V/s for the cyclic voltammetric experiment. Measurements were made using a conventional three electrode cell configuration. The platinum electrode surface was $7.85 \times 10^{-3} \text{ cm}^2$

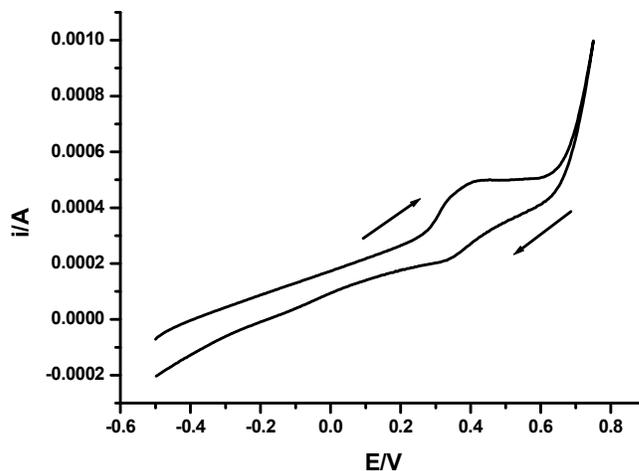


Figure 1. Cyclic voltammogram of charge transfer complex of 4,4'-bipyridine with benzoquinone derivative at platinum electrode, sweep rate 0.5 Vs^{-1} , $T = 25^\circ\text{C}$

as a working electrode, coiled platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. The potential was calculated with relative to the Ag/AgCl reference electrode at 25°C and 0.1 mol/L tetraethylammonium chloride (TEACl) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and iR compensation to minimize double-layer charging current and solution resistance.

The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rate ranging from 0.02 to 5 V/s in non aqueous media at $(25 \pm 2)^\circ\text{C}$.

Digital simulation of the data for cyclic voltammetric experiments was performed on PC computer using EG & G condosim software package. The simulation procedure was carried out using finite differences techniques. Algorithms for the simulation program were coded and implemented into the condosim software package supplied by EG & G. All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry of 4,4'-bipyridine with benzoquinone CT complex

To study the redox properties of 4,4'-bipyridine with benzoquinone, we carried out cyclic voltammetry (CV) and convolutive voltammetry measurements in dimethylformamide (DMF) solution at room temperature with tetraethylammonium chloride (TEACl) as supporting electrolyte. Fig. 1 exhibits an example response of the cyclic voltammogram of the 4,4'-bipyridine with benzoquinone at sweep rate of 0.5 Vs^{-1} recording in 0.1 mol/L tetraethylammonium chloride (TEACl) at platinum electrode.

The recorded cyclic voltammogram displayed a single anodic peak ($E_{pa} = 0.451 \text{ V}$) associated with an cathodic peak ($E_{pc} = 0.323 \text{ V}$) at 25°C (Figure 1). The two coupled peaks indicate a moderate fast chemical reaction following a quasi-reversible electron transfer (EC mechanism) [23]. In the selected range of scan

rates (0.05 –2 V s⁻¹), the difference in the peak potentials separation ($\Delta E_p = E_{pc} - E_{pa}$) is varies between 120.5 to 220.5 ± 5 mV which is more than the expected value (58 mV) for one-electron Nernstian process [24]. This may be attributed to the quasi-reversibility rate of electron transfer in addition to some uncompensated solution resistance of the DMF solution [25]. The formal potential (E^0) was determined from the average values of the peak potentials position observed in the voltammograms recorded at different scan rates (Table 1). The standard heterogeneous rate constant (k_s) was calculated from the voltammograms *via* peak separation using ΔE_p values *versus* rate constants [26]. Values of $E_p - E_{p/2}$ (Table 2) was used for calculation of the transfer coefficient (α) *via* equation (1) and found to be 0.35 ± 0.01.

$$E_p - E_{p/2} = 48/(\alpha n_a) \quad (1)$$

where E_p is the anodic peak potential and $E_{p/2}$ is the half-peak potential, *i.e.* the magnitude of the potential at half-height of peak current. After background subtraction and correction for the uncompensated resistance, the diffusion coefficient D was determined from equation 2 [24],

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} S C^{\text{bulk}} D^{1/2} \nu^{1/2} \quad (2)$$

where i_p is the peak current, n is the number of electrons consumed in electrode reaction, α is the transfer coefficient, n_a is the number of electrons participating in the rate determining step, S is the electrode surface area, C^{bulk} is the bulk concentration of the species, $D^{1/2}$ is the square root of the diffusion coefficient and $\nu^{1/2}$ is the square root of the scan rate. The estimated D value was found to be $3.12 \pm 0.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

3.2. Convolution-deconvolution voltammetry

Convulsive voltammetry has been successfully applied to analysis of mechanism of several electrochemical processes [27- 33]. The diffusion coefficient of the investigated complex was determined, after applying background subtraction and correction for uncompensated resistance, from equation 3, [28].

$$I_{\text{lim}} = n F S D^{1/2} C^{\text{bulk}} \quad (3)$$

where I_{lim} is the limiting value achieved for I_1 when the potential is driven to a sufficiently extreme value past the peak, and the other terms has their usual meanings. The diffusion coefficient was also determined from a simple and accurate method *via* combination between the definition of both limiting convoluted current and peak current of the cyclic voltammogram using equation 4 [29].

Table 1. Values of the kinetic parameters obtained for 4,4'-bipyridine with benzoquinone complex at a platinum electrode using cyclic voltammetry (CV), convolution (Conv), deconvolution (Decon) voltammetry, and digital simulation (Sim) techniques

Technique	$k_s \times 10^{-3}$ (cm s^{-1})	E^0 / V	$D \times 10^5$ ($\text{cm}^2 \text{ s}^{-1}$)	A	$k_c \text{ s}^{-1}$
Sim	3.55	0.385	3.18	0.43	0.210
CV	3.50	0.387	3.12	0.44	---
Conv.	---	---	3.25(a) 3.29(b)	---	0.220
Decon.	---	0.383	3.27	---	---

(a) value of D calculated using Eq. 3, (b) value of D calculated using Eq. 4

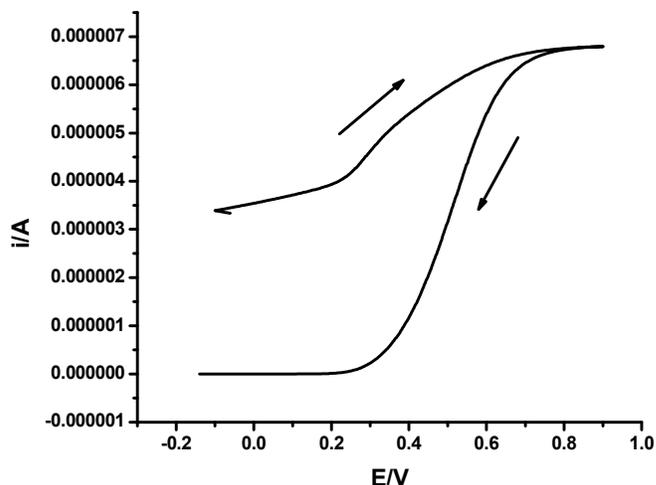


Figure 2. Convoluted current of investigated CT complex at platinum electrode, sweep rate 0.5 V s⁻¹, T = 25 °C.

$$I_{\text{lim}} = i_p / 3.099 (\alpha n_a \nu)^{1/2} \quad (4)$$

where i_p was defined in equation 2, and the other parameters have their usual meanings. The I_1 convolution of the investigated charge transfer complex illustrated in Figure 2 shows a distinct separation between the forward and reverse sweep and clearly indicates the sluggishness of electron transfer of the redox process. At low sweep rate, the reverse sweep of the I_1 convolution does not return to zero due to chemical reaction appears at longer time scales of the experiment. Values of the diffusion coefficient D evaluated *via* equations 3 and 4 are listed in Table 1. The homogeneous chemical rate constant (k_c) of the chemical step that follows the charge transfer one can be calculated *via* the kinetic convolution (I_2) at a sweep rate of 0.5 V s⁻¹, which presented in Figure 3 and calculated from the appropriate value of the chemical rate constant obtained by inserting trial value of the homogeneous chemical rate constant (k_c) into the convolution calculation until I_2 returned to zero immediately after the peak [33]. This is merely a reflection of the absence of the reductive species at the electrode at potentials before the peak when the bulk concentration of this species is zero. The true k_c value determined from I_2 convolution was found to be 1.9 s⁻¹ which agrees with the value used in simulated cyclic

Table 2. Peak characteristics of the investigated 4,4'-bipyridine with benzoquinone complex extracted from cyclic voltammetry, deconvolution voltammetry and digital simulation techniques at 0.5 V s⁻¹.

$E_p - E_{p/2} / \text{mV}$	84(a)	85(c)
$E_p - E^0 / \text{mV}$	86(a)	86(c)
W_p / mV	124(b)	123 (c)
$\Delta E_p \text{ deconv.} / \text{mV}$	82(b)	81(c)
$E_{pf} / e_{pb} \text{ (Deconv)}$	1.15 (b)	1.18(c)

(a) Values determined from CV, (b) values determined from deconvolution and (c) values determined from digital simulation.

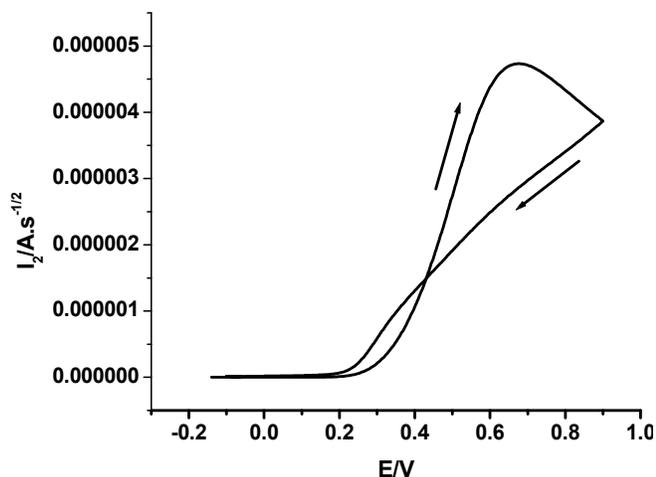


Figure 3. Kinetic convoluted current I_p of CT complex at platinum electrode, sweep rate of 0.5 V s^{-1} , $T = 25^\circ\text{C}$.

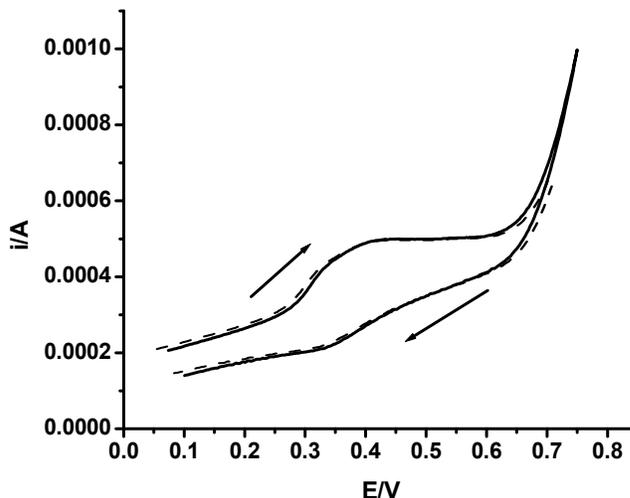


Figure 4. Matching between experimental (—) and simulated voltammograms (.....) of CT complex at a sweep rate of 0.5 V s^{-1} and $T = 25^\circ\text{C}$

voltammograms.

The diffusion coefficient was also determined from deconvolution using equation 5, [30].

$$e_p = \frac{\alpha n^2 F_2 \nu C^{\text{bulk}} D^{1/2}}{3.367 RT} \quad (5)$$

where e_p is the peak height (in Ampere) of the forward deconvolution sweep and the remaining terms have their usual meanings. Value of the diffusion coefficient estimated from this method is given in Table 1.

Also from combination between convolution and deconvolution transforms the following relationship was deduced:

$$n = \frac{ep3.367RT}{\alpha F \nu I_{\text{lim}}} \quad (6)$$

$$n = \frac{0.086ep}{I_{\text{lim}} \alpha \nu}$$

where n is the number of electrons consumed in electrode reaction, and the other parameters have their usual definitions. From equation 6 the number of electrons consumed in the electrode reaction was calculated and found to be 1.11 *ca.* 1. As shown the number of electrons was determined without knowing the electrode surface area which considers a good, precise and simple method for determining the number of electrons consumed in electrode reaction.

3.3. Digital simulation

Digital simulation of the data for cyclic voltammetric experiments was performed on PC computer using EG & G Condesim software package. The machine was programmed in Pascal. The simulation procedure was carried out using finite differences techniques [34–36]. Algorithms for the simulation program were coded and implemented into the Condesim software package supplied by

EG & G. A direct test of the determined electrochemical parameters was performed by generating the simulated cyclic voltammogram of 4,4'-bipyridine with benzoquinone complex using the average values of electrochemical parameters extracted experimentally and comparing it with the voltammogram recorded experimentally. Figure 4 shows a good agreement between the simulated and experimental voltammograms at a scan rate of 0.5 V s^{-1} verifying a moderately fast chemical step preceded by a single quasi-reversible electron transfer of the investigated complex.

4. ACKNOWLEDGEMENT

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