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Electrooxidation of congo red at glassy carbon electrode in aqueous solution

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ABSTRACT

Congo red is a symmetrical azo dye. Its exhibited color is pH-dependent and as such it has been used in chemistry as a pH indicator. This compound was electrolyzed in an aqueous solution at a Glassy Carbon Electrode (GCE) using 0.15M KCl as supporting electrolyte. Under the experimental conditions used in this study, Congo red was found to undergo a one-electron, diffusion-controlled and totally irreversible oxidation reaction. Its pertinent electrochemical parameters such as the number of electrons involved in the oxidation reaction, n, the apparent redox potential, $E^{\circ\prime}$, the diffusion rate constant, D, the heterogeneous electron transfer rate constant, k_s, and the current function were determined by cyclic voltammetric (CV) technique. These parameters were used in the determination of the reaction mechanism, which was EC_2. The product formed after electrochemical oxidation was found to undergo a disproportionation reaction in accordance with literature observation.

KEYWORDS

Congo red;
Disproportionation;
Diffusion rate constant;
Heterogeneous electron transfer.

INTRODUCTION

Congo red, whose chemical structure is shown in figure 1, is a symmetric, sulfonated azo dye and belongs to the class of protein-binding dyes. The color of the solution of Congo red is pH-dependent. At pH up to 3 this solution is bluish and at pH above 5 the color becomes bright red. As a result it has been used in Chemistry as a pH indicator[1,2]. Congo red is also used as a dyeing agent in textile industry[3-5]. Perhaps, the greatest use of Congo red is in biology and histochemistry. Under a polarized light Congo red is birefringent[6,7]. Congo red is known to bind to amyloid proteins and its birefringence under a polarized light is a characteristic[8-12] feature that has made it useful in characterizing its interaction with amyloid formation in Alzheimer patients[13]. The interaction, formation, binding, detection and aggregation of amyloid proteins have been carefully studied by spectroscopy and computer analysis[14-28] with the aid of Congo red. Congo red is known to bind specifically to the β-conformation[29,30] of amyloids even though there is mounting disagreement of this fact.

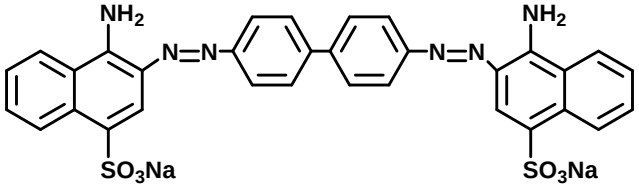

Figure 1 : The structure of congo red

TABLE 1 : Observed electrochemical parameters of congo red

Parameter	Value
n	1.0
αn_a	0.31
D	1.72×10^{-6} cm^2/s
E°'	0.63V
k_s	2.35×10^{-5} cm/s
k_2	4.48×104 M^{-1}s^{-1}

The electrostatic binding of Congo red to other forms of protein, such as the cytoskeletal, prion, insulin, etc.[31] and the study of its interaction with the α-form of these proteins have been carried out to demonstrate that it does not bind specifically to the β-amyloid fibrils[32,33]. In addition to the binding of amyloid proteins this compound has also been used in medicine[17,34] and in chemical catalysis[35,36]. Congo red in solution is known to form aggregates involving $\pi \rightarrow \pi$ stacking. It may therefore be useful as a supramolecule. However, in order to use it as a supramolecule it is necessary to fully characterize its electrochemical properties. Such electrochemical properties include the number of electrons in its oxidation reaction, n, the diffusion coefficient, D, the apparent redox potential, E°, and the heterogeneous rate constant, k_s, as well as the plausible reaction mechanism at the electrode. This becomes the theme of this work.

EXPERIMENTAL

Materials

Congo red and potassium chloride were obtained from Fisher Scientific and were used as received.

Instrument

The instrument used for all electrochemical measurements was a Cypress System's Electrochemical Analyzer. The working electrode was a glassy carbon electrode of surface area of 7.85×10^{-3}cm^2 supplied by the same company. The counter electrode was a wound platinum wire and the reference electrode was a commercial calomel electrode.

Methodology

Unless otherwise specified, all electrochemical measurements used cyclic voltammetric (CV) technique. The solutions (5.0 mM Congo red with 0.15 M KCl) were prepared using triply distilled and deionized water from Photronix Reagent Water System. In all experiments a 10.0 mL solution were electrolyzed at different sweep rates varying from 20.0 mV/s to 1.0 V/s. All measurements were made at room temperature, 25 ± 0.2°C.

TABLE 2 : The obtained current function data at different scan rates

Scan rate, V/s	Current, A	Current function, A/(V/s)$^{1/2}$
0.02	1.1705×10^{-6}	8.28×10^{-6}
0.05	1.80×10^{-6}	8.05×10^{-6}
0.10	2.54×10^{-6}	8.03×10^{-6}
0.20	3.66×10^{-6}	8.18×10^{-6}
0.25	4.00×10^{-6}	8.00×10^{-6}
0.50	5.82×10^{-6}	8.23×10^{-6}
0.80	7.53×10^{-6}	8.41×10^{-6}
1.00	8.36×10^{-6}	8.36×10^{-6}

RESULTS AND DISCUSSION

We show in figure 2 the voltammogram of 5.0mM Congo red obtained at a scan rate of 50.0 mV/s. As can be seen in this figure, there is no observable peak on the reverse scan. This implies that the compound undergoes an irreversible reaction at the electrode.

Determination of n

The number of electrons involved in the oxidation of Congo red was determined using chronoamperometry (CA). The Cottrel equation (equation1) was used in the analysis of the data.

$$i = nFAD^{1/2}C_o/(\pi t)^{1/2} \quad (1)$$

In this equation, i is the observed current during the oxidation, n is the number of electrons involved in the reaction, F is the Faraday constant, A is the working electrode surface area. D is the diffusion coefficient that was determined as discussed below. C_o and t are the bulk solution concentration and time of electrolysis, respectively. Figure 3 shows the chronoamperogram obtained and the data from there were treated by plotting i as function of $1/t^{1/2}$ in accordance with equation 1 and n was extracted from the slope of the straight line plot (Figure 4). A value of n of approximately 1 was obtained and this is used in subsequent calculations.

Determination of heterogeneous rate constant, k_s, the redox potential, E°, and the electron transfer coefficient, α_n

A series of scan rates varying from 0.02 V/s to

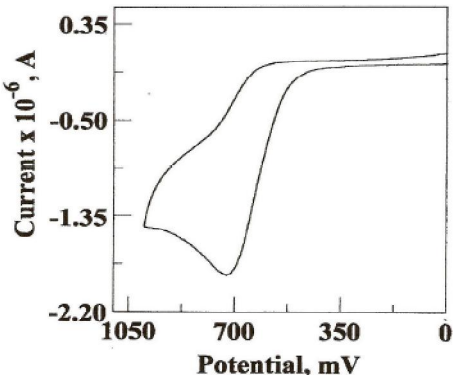

Figure 2 : The voltammogram of 5.0mM congo red at scan rate of 50.0mV/s

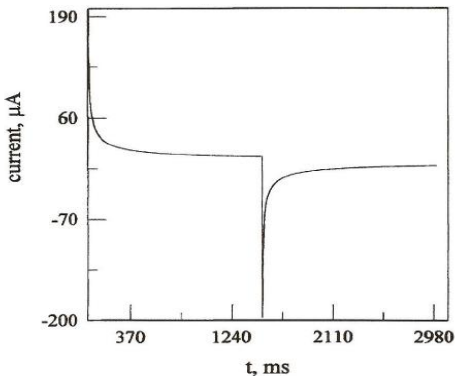

Figure 3 : The amperogram of 5.0mM congo red

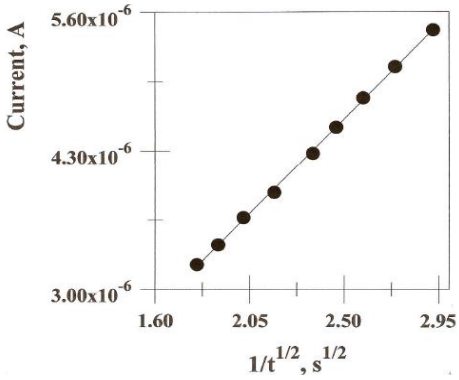

Figure 4 : The cottrell plot of 5.0mM of congo red

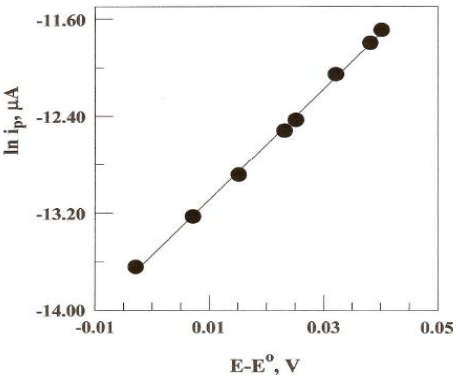

Figure 5 : Plot of the Ln of the observed current versus the observed peak potential minus the determined redox potential

1.0 V/s were performed and the logarithm of the current obtained at each scan rate was plotted as function of the observed peak potential minus the redox potential (E-E°) in accordance with the literature methodology[37].

$$i_p = 0.227nFAC_o k_s e^{[(-\alpha naF)(E-Eo)]/RT} \quad (2)$$

In this equation, i_p is the peak current, n is the number of electrons involved in the reaction, F is the Faraday constant, A is the surface area of the working electrode, k_s is the heterogeneous rate constant, and R and T are the universal gas constant and temperature, respectively. The resultant plot was seen to be linear. However, initially, the E° was set at 0.40 V, at the foot of the voltammogram as suggested by Reinmuth[38]. The k_s thus obtained was inserted into the equation of Nicholson[39] which is given below (equation 3) to obtain another relative E°. These values of E° and k_s were iterated in equations 2 and 3 until their convergence.

$$E_p = E°-(RT/3nF)\ln[(4.78\pi 3D_o/2D_R)]-(RT/3nF)\ln(nF/RTk_sC_o) \quad (3)$$

In this equation E_p and E° are the observed peak potential and redox potential, respectively, while the D_o and D_s are the diffusion coefficients of the oxidized and reduced species of Congo red, respectively. However, the value D_o/D_s is assumed to be unity in this work. The remaining symbols have their usual electrochemical meanings. The final plot of ln i_p versus the obtained E-E°, which, as can be seen, is linear, is shown in figure 5. The k_s and αn_a were extracted from the intercept and slope, respectively, in accordance with equation 2. The values are 2.35 x 10^{-5}cm/s and 0.31, respectively. All the obtained parameters are listed on TABLE 1.

The experimental parameters so far determined showed that Congo red undergoes an irreversible charge transfer in its oxidation reaction. The diagnostic criteria used to reach such conclusion include the following: a) there is no observable peak in the reversal of the cyclic voltammogram; b) the observed oxidative potential shifts anodically by a rate of 26mV per decade increase in scan rate as can be seen in figure 6c) the current function is independent with scan rate as can be seen in TABLE 2.

Determination of diffusion coefficient, D

Scan rate studies that were made of this compound

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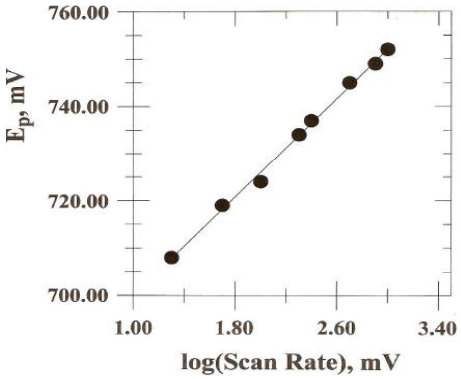


Figure 6 : The plot of the observed peak potential versus the logatithm of scan rate for 5.0mM congo red

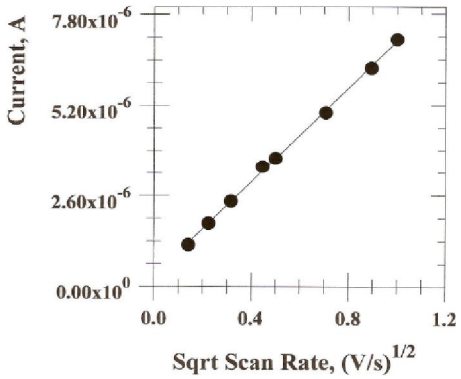


Figure 7 : The plot of the observed current versus the square root of scan rate for 5.0mM congo red

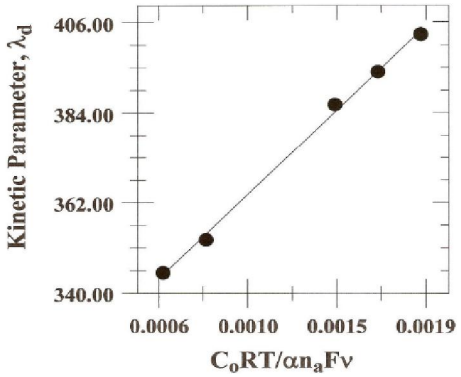


Figure 8 : Plot of the kinetic parameter versus the initial concentration times the time frame of the voltatammety of congo red for the determination of k_2

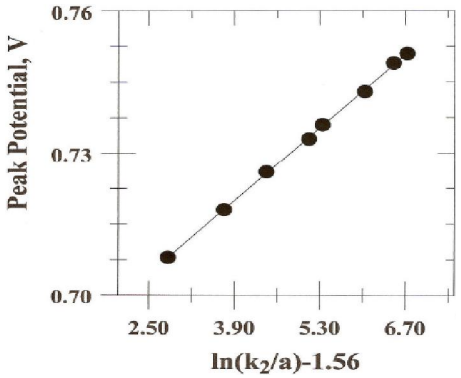


Figure 9 : Plot of the observed peak potential vesus the determined kinetic parameter

vary from 20.0mV/s to 1.0 V/s. The observed current when plotted with the square root of the scan rate gives a slope that is proportional to the $D^{1/2}$ from which the diffusion coefficient of $1.7 \times 10^{-6}cm^2/s$ was obtained in accordance with equation 4.

$$i_p = 2.699 \times 10^5 nA (\alpha n_a)^{1/2} C_o \nu^{1/2} D^{1/2} \quad (4)$$

The i_p in this equation is the observed peak current and the α is the electron transfer coefficient as discussed above. As can be seen a plot of i_p versus $\nu^{1/2}$ is linear (Figure 7). The slope of this linear plot is used to determine the diffusion coefficient, D. The value of D, $1.7 \times 10^{-6}cm^2/s$, thus obtained is in good agreement with the literature value of $2.0 \times 10^{-6}cm^2/s$[40-42]. The observations made so far are consisted with an EC_2 mechanism as given by Bard and Faulkner[43] and may be represented by the following scheme:

$$R \leftrightarrows R^{\bullet} + e^-$$
$$2R^{\bullet} \rightarrow R_2$$

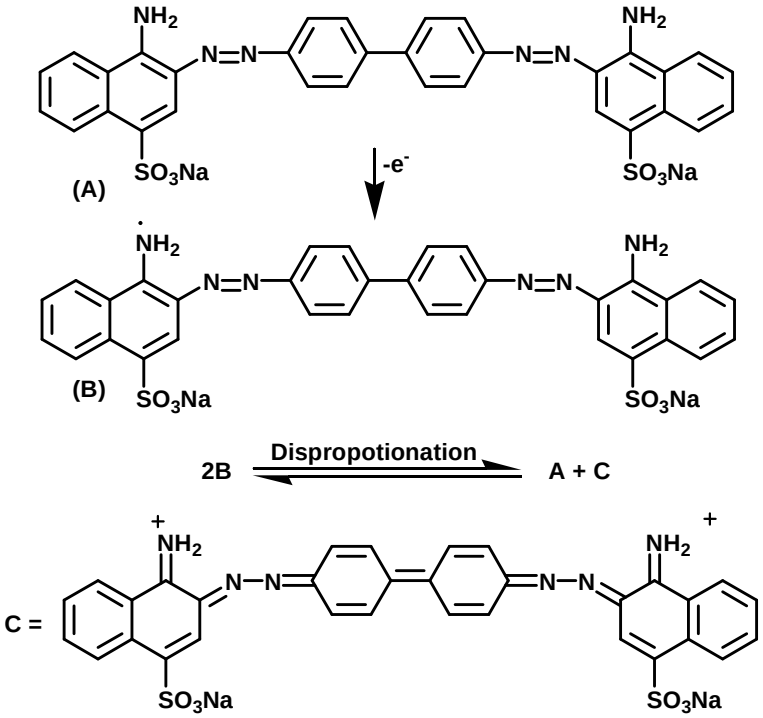
Scheme 1

However, it is known that congo red undergoes a disproportionation reaction[44,45] and using the paradox of disproportionation enunciated by Feldberg[46], we propose that theEC_2 voltammetric oxidation of congo red to produce a metastable radical undergoes a kinetically controlled disproportionation reaction to produce the starting material and a dication, according to Scheme 2.

$$R \xrightarrow{-e^-} R^{\bullet}$$
$$R^{\bullet} \underset{}{\overset{k_2}{\rightleftharpoons}} R + R^{++}$$

Scheme 2

Saveant and his co-workers[47] have given a thorough theoretical treatment for an EC disproportionation reactions. We have used the working curve presented in that work to determine the kinetic parameter, λ_d, (KP) for our work. In that work also (equation 101) they showed that $\lambda_d = k_d C_o RT/\nu nF = k_d C_o/a$. k_d in this equation is equal to k_2 and is the disproportionation rate constant and C_o is the initial concentration for a given scan rate. a is $\alpha n_a F\nu/RT$ and the terms therein have their usual electrochemical meanings. Therefore a plot of KP versus C_o/a will be seen to be linear. The curve thus obtained is shown in fig-



Plausible voltammetric reaction mechanism of congo red

Scheme 3

ure 8. As can be seen from this figure a linear curve was obtained. The slope of this straight-line plot was used to obtain the desired second order disproportionation rate constant, $k_d = k_2$. The value of k_2 thus obtained was $4.79 \times 10^4 M^{-1}s^{-1}$. The kinetic parameter obtained as per the working curve stated above was plotted against the peak potential obtained at different scan rate in the voltammetric oxidation of Congo red in accordance with equation 5[48].

$$E_p = E° + RT/2nF\ [\ln(k_2/a) - 1.56] \quad (5)$$

In this equation, a and the rest terms are as defined above. A perfect straight line curve was obtained as can be seen in Fig. 9 with a correlation coefficient of 0.9998. The intercept which is E^o gave a value of 0.67 V which can be compared with that obtained as given in section 3.2 (0.63 V). With this observation we give below what we thought to be a plausible voltammetric oxidation reaction mechanism for Congo red at a glassy carbon electrode which is consistent with that given by Corio and his co-workers[44].

CONCLUSION

We have shown that Congo red undergoes a-1e- irreversible, diffusion controlled oxidation reaction at GCE. The mechanism of the reaction is of the EC_2 type. The oxidation product undergoes a disproportionation reaction to produce the starting material and a dication. The relevant electrochemical parameters were determined as well as the second order rate constant associated with this disproportionation.

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