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Electrochemical Oxidation of Catechol in the Presence of some Azacrown Ethers and Transition Metal Ions in Acetonitrile

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The electrochemical oxidation of catechol (H_2Q) (**1**) has been studied in the absence and presence of 1,10.diaza-18-crown-6 (DA18C6) (**2a**), 1,7-diaza-15-crown-5 (DA15C5) (**2b**) and aza-15-crown-5 (A15C5) (**2c**) and also, in the presence of some transition metal ions (Zn^{2+}, Ni^{2+} and Cd^{2+}) in acetonitrile containing tetra-*n*-butylammonium perchlorate as supporting electrolyte, by means of cyclic voltammetry. The results indicate an *ECCE(E)C* mechanism in electrochemical oxidation of catechol (H_2Q) (**1**) in the presence of azacrown ethers **2a-c**. The cyclic voltammetric data were analyzed by digital simulation to confirm and to measure the homogeneous parameters for the suggested electrode mechanism. The calculated observed homogeneous rate constants (k_{obs}) for the reaction of electrochemically generated cation radical ($H_2Q^{\bullet+}$) with azacrown ethers **2a-c** was found to vary in the order DA18C6 >DA15C5 >A15C5.

Keywords: Azacrown ether, Catechol, Digital simulation, Homogeneous rate constant, Transition metal ions, Cyclic voltammetry

1. INTRODUCTION

The crown ethers are the most popular host compounds in host-guest chemistry field, which have shown a remarkable ability to form strong complexes with metal and organic cations [1]. The synthesis and cation complexing characteristics of a number of crown ethers were first reported by Pedersen [2]. Since that time, a large number of normal crown ethers and multisided crown ethers have been prepared and their cation complexing properties have been studied [3-10]. Metal cations exactly fitting the size of the crown ether unit form a host/guest 1:1 complex; when the cation size exceed that of the crown cavity, the cation can only partially fit, and, as a result, a sandwich-type structure can be formed [11-14]. Complexation of crown ethers with metal cations depends on many factors, such as the cavity size, the nature of heteroatoms (oxygen, nitrogen and sulfur) and substituent in the macrocycle and the solvent. The fitness of the cavity size of a macrocyclic compounds is an important factor for determining the stability of metal complex [15]. The complexation of transition metal ions has been studied mainly with respect to aza and thia crown ethers, but not with oxa crown ethers [16]. The azacrowns have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex alkali and alkaline earth metal ions, and those of the all-nitrogen cyclams, which strongly complex heavy-metal cations [17]. On the other hand, it is shown that, the electrochemically generated *o*-benzoquinones are quite reactive intermediate which in aqueous solutions, can be attacked by a variety of nucleophiles and undergo various mechanisms such as EC [18-21], ECE, [22-24] ECEC [25-27], ECECE [28,29], ECECEC [30], ECECECE [31], ECEC2 [32], and trimerization [33] convert to final products. The mechanism is depending on some parameters such as, nature of nucleophile (electron withdrawing or donating), electrolysis medium (solvent, acidity or pH) and catechol type. A literature survey reveals that, in contrast to these vast number reports on electrochemical oxidation of catechols in the presence of nucleophiles in aqueous solutions [18-33], no paper has reported on the electrochemical oxidation of catechols in the presence of nucleophiles in nonaqueous solutions. This prompted us to investigate the electrochemical oxidation of catechol (H_2Q) (**1**) in the presence of azacrown ethers **2a-c** (Fig. 1) as nucleophiles in acetonitrile solution. The mechanistic pathway of the electrode reaction was discussed and calculated the observed homogeneous rate constants (k_{obs}) of the reaction of catechol-cation radical ($H_2Q^{\bullet+}$) with azacrown ethers **2a-c**. Furthermore, the electrochemical oxidation of a mixture of catechol (H_2Q) (**1**)/azacrown ethers (**2a-c**) in acetonitrile solutions has studied in the presence of some transition metal ions (Zn^{2+}, Ni^{2+} and Cd^{2+}) and the effect of these metal ions on electrochemical oxidation of catechol (H_2Q) (**1**) in the presence of azacrown ethers (**2a-c**) has been discussed.

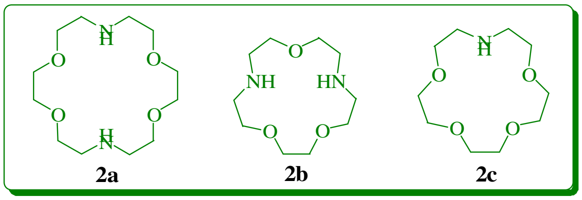


Figure 1. Chemical structure of azacrown ethers (**2a-c**).

2. EXPERIMENTAL PART

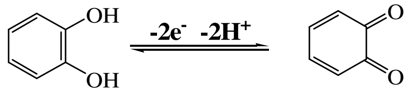
2.1. Apparatus and reagents

Reaction equipments and chemicals are described in an earlier article [23]. The homogeneous rate constants were estimated by analyzing the cyclic voltammetric responses using the simulation DIGIELCH software [34].

3. RESULTS AND DISCUSSION

3.1. Electrochemical study of catechol in the presence of azacrown ethers

Electrochemical oxidation of catechol (H_2Q) (**1**) in aqueous solutions shows one two-electron oxidation wave which corresponds to the transformation of catechol to *o*-benzoquinone as shown in Scheme 1 [35].



Scheme 1.

In contrast to the one two-electron step in aqueous solutions, in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte, catechol (H_2Q) exhibits one quasi-reversible one-electron redox couple (A_1 and C_1) at 1.00 and 0.34 V vs. Fc/Fc^+, respectively, and an irreversible oxidation peak (A_4) occurs at 1.99 V vs. Fc/Fc^+ to give a product which is reduced at -0.17 V vs. Fc/Fc^+ (peak C_4). (Fig. 2, curve a). The cathodic peak C_4 disappeared when the switching potential reduced to 1.5 V vs. Fc/Fc^+ (Fig. 2, curve b). The first couple represents a quasi-reversible oxidation of catechol (H_2Q) to the semiquinone cation radical ($H_2Q^{\bullet +}$). The formed radical cation rapidly loses a proton to form the semiquinone radical ($HQ^{\bullet}$) [36-39]. The one-electron oxidation of semiquinone radical ($HQ^{\bullet}$) followed by deprotonation completes the overall two-electron process to give the quinone (Q) which, because of its instability, appears as an irreversible peak [35]. The reduction peak that is observed at 0.34 V (peak C_1) for the reverse scan of the initial catechol oxidation peak is due to reduction of semiquinone radical ($HQ^{\cdot}$) followed by proton abstraction to give the catechol (H_2Q).

The oxidation of catechol (H_2Q) (0.5 mM) was studied in the presence of 0.5 mM diaza-18-crown-6 (DA18C6) (**2a**) as a nucleophile. Fig. 3 shows the cyclic voltammogram obtained for catechol (H_2Q) in the presence of **2a** in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte. In this condition, anodic and cathodic peaks A_1 and C_1 decreases and voltammogram exhibits two new anodic (A_2 and A_3) and cathodic (C_2 and C_3) peaks. The cation radical formed at the first oxidation step of H_2Q is unstable. If the solution contains a nucleophile or a base, the radical cation ($H_2Q^{+\bullet}$) reacts with that nucleophile or base. The product of this reaction is easier to oxidize than cation radical [40]. Thus, in the presence of DA18C6 (**2a**) as a nucleophile, the anodic peak A_3 appears at less anodic potential (0.33 V vs. Fc/Fc^+) (Scheme 2). In this condition, also, another new anodic peak (A_2) appears at potential between E_{pA1} and E_{pA3} (0.56 V vs. Fc/Fc^+). This peak (A_2) appears only in electrochemical oxidation of catechol in the presence of 1,10-diaza-18-crown-6 (DA18C6) (**2a**) and 1,7-diaza-15-crown-5 (DA15C5) (**2b**).

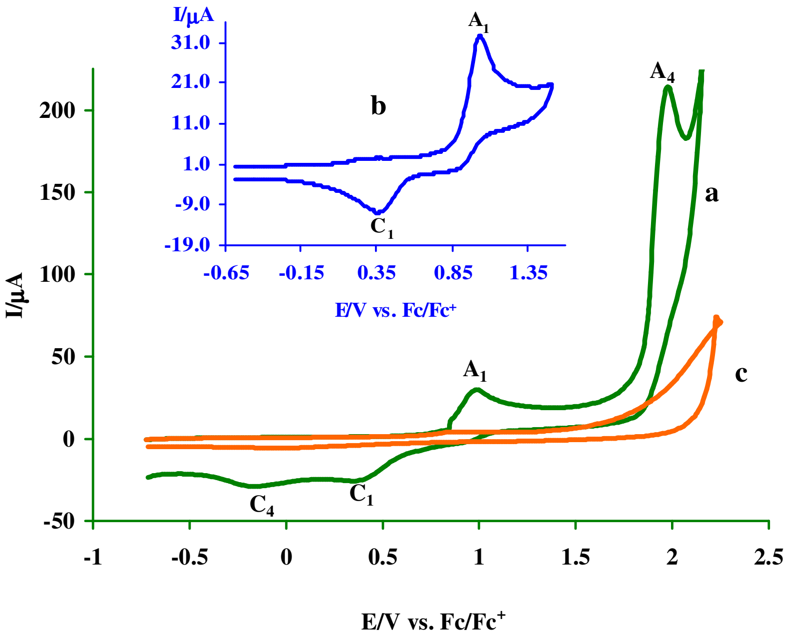
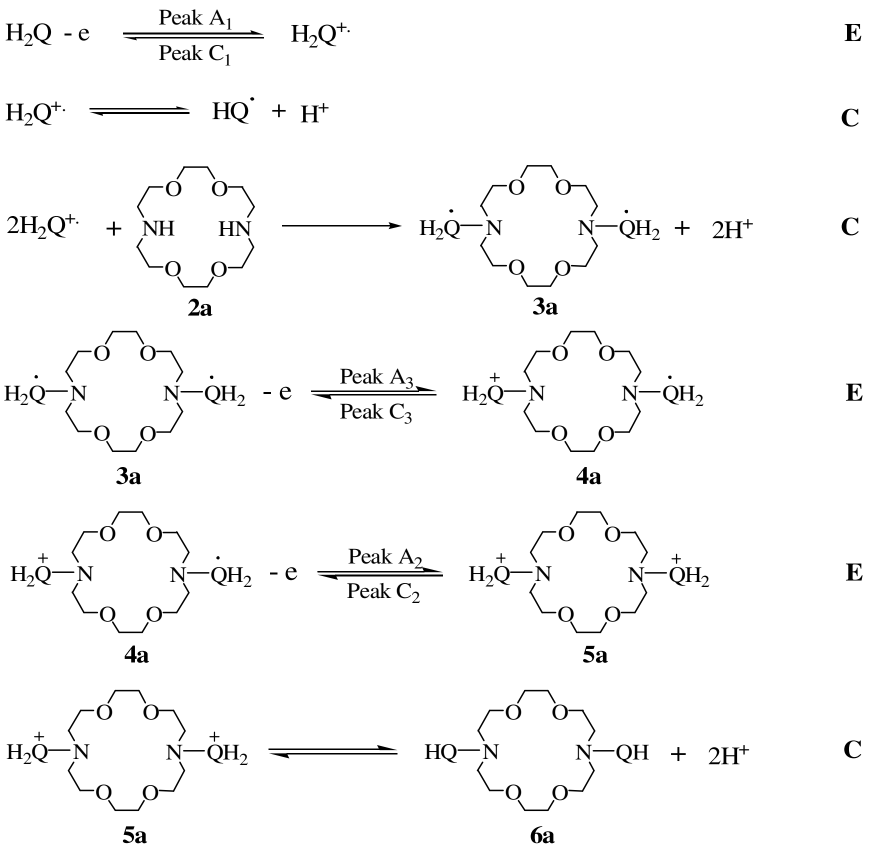


Figure 2. (a and b) Cyclic voltammograms of 0.5 mM catechol (**1**) at glassy carbon electrode, in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate. (c) Same as (a) without catechol. Scan rate: 400 mVs^{-1}. t = 25 ± 1°C.



Scheme 2.

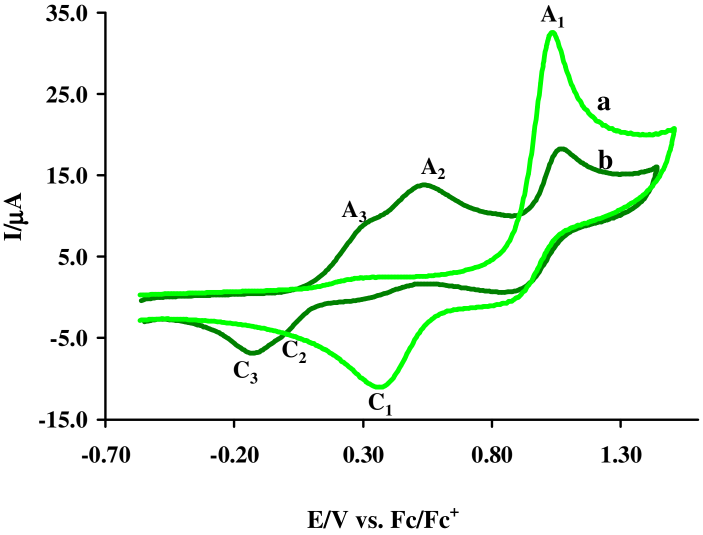


Figure 3. Cyclic voltammograms of catechol (**1**) (0.5 mM): (a) in the absence, (b) in the presence of 0.5 mM DA18C6 (**2a**) at glassy carbon electrode, in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate. Scan rate: 400 mVs^{-1}. t = 25 ± 1 °C.

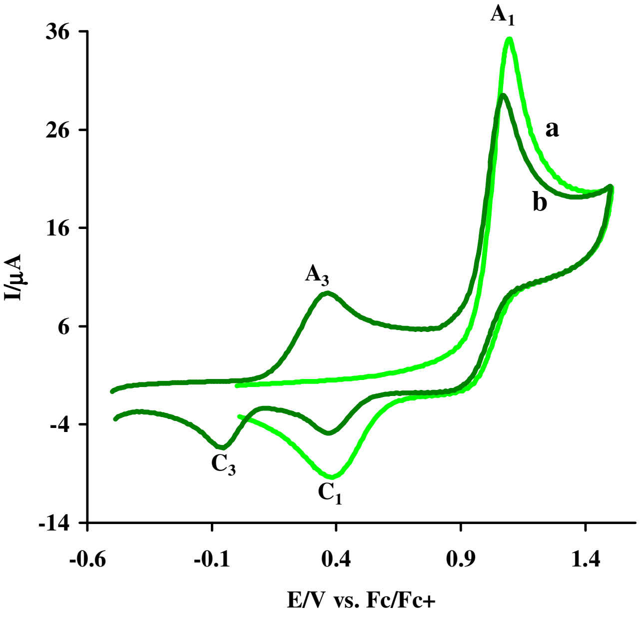
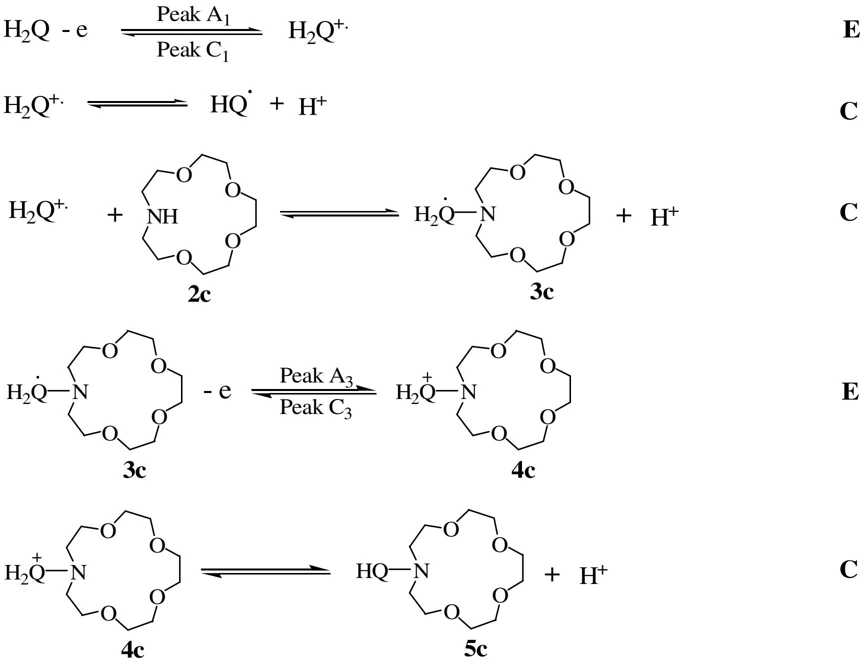


Figure 4. Cyclic voltammograms of catechol (**1**) (0.5 mM): (a) in the absence, (b) in the presence of 0.5 mM A15C5 (**2c**) at glassy carbon electrode, in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate. Scan rate: 400 mVs^{-1}. t = 25 ± 1 °C.

According to proposed mechanism, the anodic peak A_1 pertains to the oxidation of H_2Q to the $H_2Q^{\bullet+}$ and cathodic peak C_1 is its counterpart. The new anodic peaks A_2 and A_3 can be related to electrochemical oxidation of **4a** and **3a**, respectively. Clearly, the cathodic peaks C_2 and C_3 correspond to the reduction of the compounds **5a** and **4a**, respectively.

Fig. 4 shows the cyclic voltammogram obtained for catechol (H_2Q) in the presence of aza-15-crown-5 (A15C5) (**2c**) in same conditions. In this condition, anodic and cathodic peaks A_1 and C_1 decreases and voltammogram exhibits a new anodic (A_3) and its cathodic counterpart (C_3) peaks. This new anodic peak (A_3) is related to oxidation of radical $H_2Q^{\bullet}$-A15C5 (**3c**) to cation H_2Q^{+}-A15C5 (**4c**) (Scheme 3).



Scheme 3.

In continuation, the effect of some transition metal ions (Cd^{2+}, Ni^{2+} and Zn^{2+}) on the electrochemical behavior of catechol (H_2Q)/azacrown ethers has been studied. Figure 5, shows the cyclic voltammograms obtained for H_2Q in the presence of DA18C6 (**2a**) and Cd^{2+}. In this condition, anodic peaks A_2 and A_3 and cathodic peaks C_2 and C_3 disappear and peak C_1 reappears. This means that, in the presence of Cd^{2+}, because of the complexation of transition metal ions with azacrown ethers, the nucleophilicity of azacrown ethers is decreased. In the presence of Cd^{2+}, the potential of peak A_1 (E_{pA1}) and its cathodic counterpart (E_{pC1}) are shifted to negative direction. This may be related to formation of an ion-pair between nitrate ion and semiquinone cation radical (NO_3^--$H_2Q^{\bullet+}$). The same results obtained in the presence of Ni^{2+} and Zn^{2+} ions.

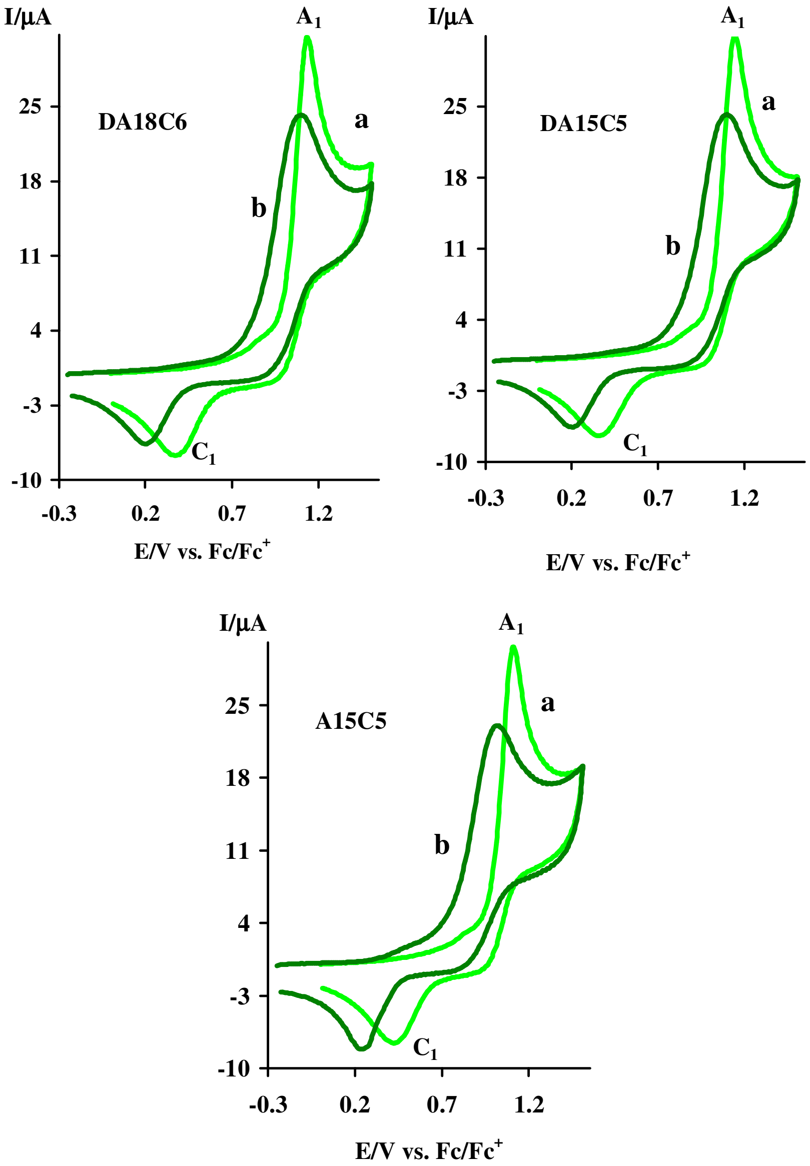


Figure 5. Cyclic voltammograms of 0.5 mM catechol: (a) in the absence (b) in the presence of 0.5 mM azacrown ethers and 0.5 mM $Cd(NO_3)_2.4H_2O$ at glassy carbon electrode in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate. Scan rate: 400 mVs^{-1}. t = 25 ± 1 °C.

4. DIGITAL SIMULATION

Digital simulation is a useful method in evaluation of complicated electrode reactions [41]. In this direction, when simulated cyclic voltammogram curves fit the experimental cyclic voltammogram curves, we can confirm the reaction mechanism and obtain thermodynamic and kinetic parameters concerning the electron transfer and chemical processes [40]. By the development of simulation softwares cyclic voltammetry has become a very powerful technique. On the contrary, without simulation software, cyclic voltammetry is not as convenient [40]. To confirm the assumed reaction mechanisms in Schemes 2 and 3, and obtaining the observed homogeneous rate constants (k_{obs}) of reaction of electrochemically generated $H_2Q^{\bullet +}$ (**1a**) with azacrown ethers (**2a-c**), the simulated cyclic voltammograms have been compared with experimental cyclic voltamograms (Fig. 6).

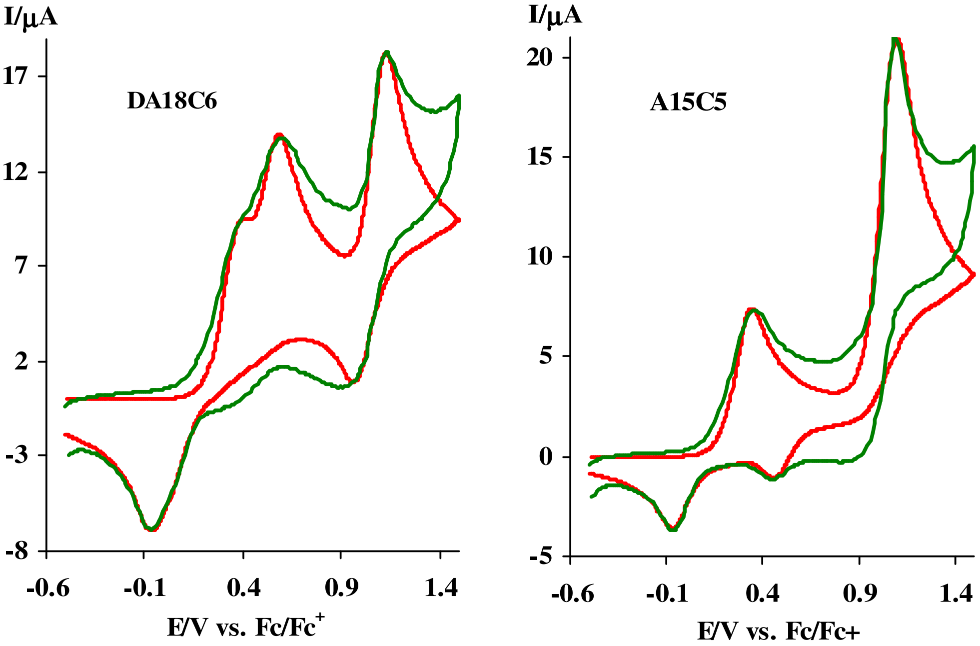


Figure 6. Experimental (green color) and simulated (red color) cyclic voltammograms of 0.5 mM catechol (**1**) in the presence of 0.5 mM DA18C6 (**2a**) and A15C5 (**2c**) at glassy carbon electrode, in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate. Scan rate: 400 mVs^{-1}. t = 25 ± 1°C.

The simulation was carried out assuming semi-infinite one-dimensional diffusion and planar electrode geometry. The experimental parameters entered for digital simulation consisted of the following: E_{start}, E_{switch}, E_{end}, t=25 °C and analytical concentration of H_2Q and azacrown ethers (**2a-c**). The transfer coefficient (α) was assumed 0.5, and the formal potentials were obtained experimentally as the average of the two peak potentials observed in cyclic voltammetry. The heterogeneous rate constant for oxidation of H_2Q were estimated by use of an experimental working curves [42]. The procedure is performed based on achieving the best fit between simulated and experimental cyclic voltammograms. The calculated values of rate constants for reaction of cation radical ($H_2Q^{\bullet +}$) with azacrown ethers (**2a-c**) have shown in Table 1. As shown in Table 1, the magnitude of observed homogeneous rate constants (k_{obs}) is dependent on the ring size of crown ether and number of nitrogen atom. DA18C6 (**1a**) and DA15C5 (**1b**) are bidentate nucleophiles (bis-donors) so that they are much better nucleophile as compared with A15C5 as a monodentate nucleophile. On the other hand, the comparison of k_{obs} in the cases of bidentate nucleophiles, DA18C6 (**1a**) and DA15C5 (**1b**) shows that the k_{obs} increases with increasing ring size of crown ether. This is most probably due to the existence of longer distance between the two nitrogen atoms in the case of DA18C6 (**1a**), exhibits better bidentate nucleophilicity and therefore, greater observed homogeneous rate constants (k_{obs}) than DA15C5 (**1b**) with shorter distance between the nitrogen atoms.

Table 1. Calculated observed homogeneous rate constants ($k_{obs}/M^{-1}s^{-1}$) for the reaction of 0.5 mM catechol (**1**) in the presence of 0.5 mM azacrown ethers **2a-c** in acetonitrile containing 0.1 M Bu_4NClO_4 at 25± 1 ºC.

k_{obs} ($M^{-1}s^{-1}$)[a]		
DA18C6	DA15C5	A15C5
200±0.10	170±0.10	70±0.04

[a] For n = 8 in various scan rates.

5. CONCLUSIONS

The results of this work show that the electrochemically generated cation radical ($H_2Q^{\bullet+}$) from the first one-electron oxidation step of catechol, is reactive and can be attacked by azacrown ethers. In this report, the mechanism of electrochemical oxidation of catechol (H_2Q) (**1**) in the presence of azacrown ethers (**2a-c**) is proposed and confirmed using digital simulation. The cyclic voltammograms were digitally simulated under *ECCEEC* (for 1,10.diaza-18-crown-6 (DA18C6) (**2a**) and 1,7-diaza-15-crown-5 (DA15C5) (**2b**) as bidentate nucleophiles) and ECCEC (for aza-15-crown-5 (A15C5) (**2c**) as a monodentate nucleophile). The simulated cyclic voltammograms show good agreement with those obtained experimentally. The magnitude of observed homogeneous rate constants (k_{obs}) is dependent on the ring size of crown ether and number of nitrogen atoms. In addition, the effect of some transition metal ions (Cd^{2+}, Ni^{2+} and Zn^{2+}) on the electrochemical behavior of catechol (H_2Q)/azacrown ethers has been studied. The results indicate that, in the presence of these metal ions, because of the complexation of azacrown ethers with them, the nucleophilicity of azacrown ethers are decreased.

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