

SHORT COMMUNICATION

Mojtaba Shamsipur · Abdollah Salimi
Seyed Mehdi Golabi · Hashem Sharghi
Mir Fazlollah Mousavi

Electrochemical properties of modified carbon paste electrodes containing some amino derivatives of 9,10-anthraquinone

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Abstract The preparation and aqueous electrochemistry of carbon paste electrodes modified by some amino-substituted 9,10-anthraquinones are reported. In all cases, the reduction processes studied by cyclic voltammetry reveal a quasi-reversible behavior. The half-wave potentials were calculated as a function of the solution pH and from the resulting potential-pH plots the formal potentials and pK'_a values of different redox and acid-base couples involved at various pH ranges were evaluated. The diffusion coefficients of different anthraquinone derivatives used in paraffin oil were calculated by chronoamperometry.

Key words Carbon paste · Amino anthraquinones · Cyclic voltammetry · Chronoamperometry · Diffusion coefficient

Introduction

Since the first invention of carbon paste electrodes (CPE) by Adams [1], they have been extensively applied to the fields of electroanalysis and biosensors [2, 3]. The broad application of CPEs is mainly based on their interesting advantages such as low cost, wide potential windows, ease of preparation and renewal, and conve-

nient modification [4]. The extensive use of CPEs modified with various electroactive compounds, and usually prepared by the direct mixing technique [5], has also been reported in the literature [6–8]. These applications involve preparation of biosensors [4–13], determination of trace amounts of elements [14–19], evaluation of electrochemical processes [6, 8, 20–23], and investigation of electrocatalytic mechanisms [8, 24–28].

9,10-Anthraquinone derivatives, as the largest group of naturally occurring quinones, are of fundamental importance both in industry [29, 30] and medicine [31–34]. Various quinones are known to possess anticancer activity [32, 34]. Bioreduction and redox cycling are supposed to play a key role in the activation of many quinone drugs under aerobic conditions [31], so that information about the redox properties of these drugs will be very helpful in understanding their mechanisms of action against various diseases [35]. Besides the widespread solution studies of the electrochemical behavior of different quinone derivatives [35–41], considerable interest has been focused on the preparation of electrodes modified by quinoidal units for catalytic purposes [21, 28, 42–44].

In recent years, we have been involved in the synthesis [45, 46], acid-base [47–49] and electrochemical studies [41, 50], and some applications in extraction and membrane transport of metal ions [51] and in the construction of ion-selective electrodes [52, 53] of some derivatives of 9,10-anthraquinone and 9-anthrone. In this work, we have prepared CPEs containing five recently synthesized amino derivatives of 9,10-anthraquinone [54], shown in Fig. 1. The electrochemical behavior of the resulting modified CPEs in various buffered aqueous solutions was investigated by cyclic voltammetry. The potential-pH diagrams of the anthraquinone derivatives used were constructed and from these diagrams the apparent standard potentials, together with the dissociation constants of intervening acid-base couples, were evaluated.

M. Shamsipur (✉)
Department of Chemistry, Razi University,
Kermanshah, Iran

A. Salimi · M.F. Mousavi
Department of Chemistry,
Tarbiat Modarres University, Tehran, Iran

S.M. Golabi
Electroanalytical Chemistry Laboratory,
Faculty of Chemistry, University of Tabriz, Tabriz, Iran

H. Sharghi
Department of Chemistry,
Shiraz University, Shiraz, Iran

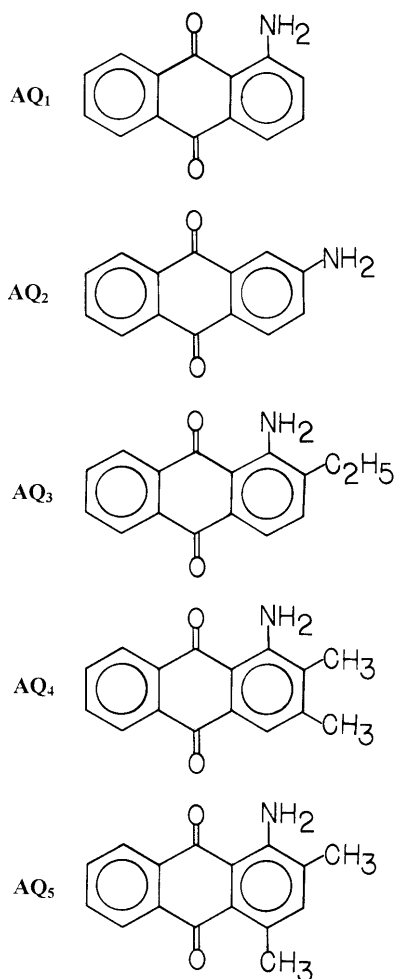


Fig. 1 Structures of the amino-anthraquinones used

Experimental

Chemicals

1-Amino-9,10-anthraquinone (AQ₁), 2-amino-9,10-anthraquinone (AQ₂), 1-amino-2-ethyl-9,10-anthraquinone (AQ₃), 1-amino-2,3-dimethyl-9,10-anthraquinone (AQ₄), and 1-amino-2,4-dimethyl-9,10-anthraquinone (AQ₅) were synthesized [54] and used after recrystallization from reagent grade benzene (Merck) and vacuum drying (Fig. 1). HPLC grade acetonitrile (Fluka) was used as received. Triply distilled deionized water was used throughout. The buffers used at different pH were 0.1 M H₂SO₄ + NaOH (for pH = 0.5–1.5), 0.1 M H₃PO₄ + NaOH (for pH = 2.0–3.0), 0.1 M acetate buffer (for pH = 3.5–6.0) and 0.1 M NaH₂PO₄ + NaOH (for pH = 6.5–13.0). All of the chemicals used were reagent grade (Fluka or Merck) and were used as received. N₂ gas with a purity of 99.999% was used to deaerate the solutions during the experiments.

Electrode preparation

A 3% (w/w) anthraquinone-spiked graphite powder (spectroscopic grade, Merck) was made by thorough mixing of an appropriate amount of the anthraquinones AQ₁–AQ₅ with 200 mg graphite. Then 100 µg paraffin (Fluka) was added and mixed well. The resulting anthraquinone-spiked carbon paste was then inserted into

the bottom of a plastic tube having an internal diameter of 3 mm. A copper wire was inserted into the carbon paste to implement the electrical conduction. The CPEs were finally smoothed manually by a clean filter paper.

Apparatus

The electrochemical measurements were carried out at a thermostated temperature of 25.0 ± 0.1 °C. A three-electrode system consisting of a Pt wire counter electrode, an Ag/AgCl (satd), 3 M KCl reference electrode, and a modified carbon paste working electrode was employed. A Metrohm multipurpose instrument model 693 VA Processor with a 694 VA Stand and a thermal printer was used for all measurements.

Results and discussion

The electrochemical properties of the modified CPEs containing different amino-anthraquinone derivatives were investigated by cyclic voltammetry in aqueous buffered solutions. Figure 2 shows the cyclic voltammograms corresponding to a free and an anthraquinone-spiked CPE in deoxygenated aqueous 0.5 M H₂SO₄. As seen, over a potential range of 600 to –600 mV, the cyclic voltammogram of the carbon paste containing AQ₅ shows a single reduction peak and a corresponding oxidation peak. However, the free CPE shows no peaks at this potential range. The CPEs modified with other amino-anthraquinone derivatives revealed similar electrochemical behavior.

Figure 3A shows the cyclic voltammograms of a CPE containing anthraquinone AQ₁ recorded at

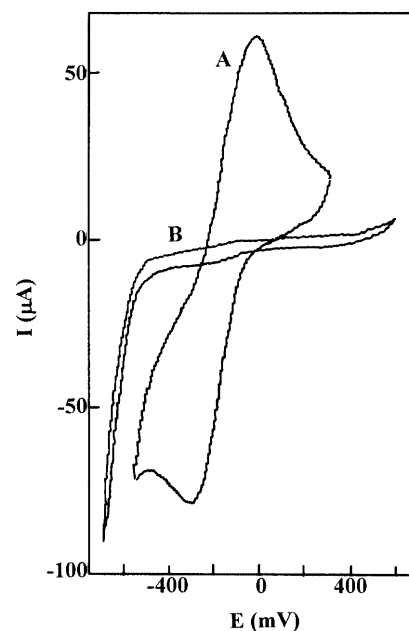


Fig. 2 Cyclic voltammograms of A the carbon paste electrode (CPE) spiked with AQ₂ and B free CPE in deoxygenated aqueous 0.5 M H₂SO₄

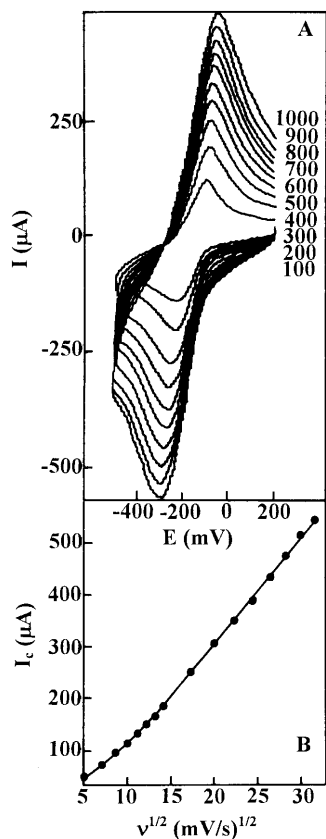


Fig. 3 A Cyclic voltammograms of the CPE spiked with AQ₁ at various scan rates in 0.5 M H₂SO₄ solutions. The scan rates (mV s⁻¹) are given on the plots. B The corresponding I_{pc} vs. $v^{1/2}$ plot

various scan rates in an aqueous 0.5 M H₂SO₄ solution. The corresponding cathodic peak current-(sweep rate)^{1/2} plot is also shown in Fig. 3B. The CPEs spiked with other amino-anthraquinones used also resulted in similar electrochemical behavior. As seen from Fig. 3B, I_c is linearly proportional to $v^{1/2}$ at higher sweep rates, while some curvature is observed at sweep rates lower than about 100 mV s⁻¹. A similar trend has also been reported for CPEs modified with metalloporphyrins [25] and naphthoquinone derivatives [25], emphasizing that the diffusion of the modifier molecule from the paraffin oil to the carbon electrode surface obeys a linear semi-infinite diffusion law on the voltammetric time scale.

The ΔE_p (i.e. $E_{pc} - E_{pa}$) values evaluated from the cyclic voltammograms of the modified CPEs tested (see Fig. 2A) were about 40 mV at low scan rates of around 10 mV s⁻¹ and increased by increasing scan rate, indicating the occurrence of quasi-reversible reductions. Moreover, in all cases, the peak current ratio (I_{pa}/I_{pc}) was found to be greater than unity. This is most probably indicative of some kinetic or other complications in the electrode process [21, 55].

Electrochemical properties of the amino-anthraquinone modified carbon CPEs prepared in aqueous buffered solutions over a pH range of 1–13 in the absence of

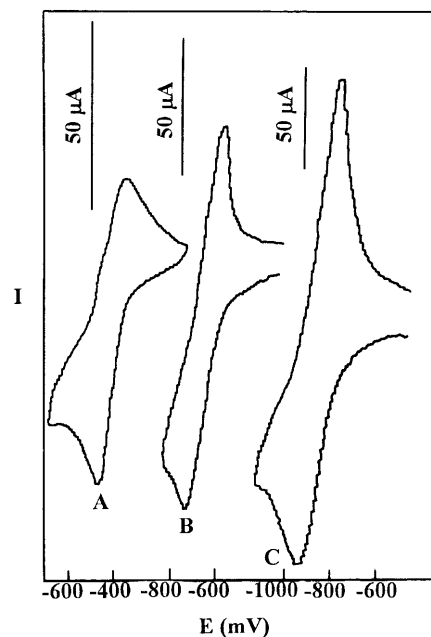


Fig. 4 Cyclic voltammograms of the CPE spiked with AQ₁ at pH 3 (A), 7 (B), and 12 (C). The scan rate is 50 mV s⁻¹

dioxygen were investigated by cyclic voltammetry. Sample cyclic voltammograms at various pH values are shown in Fig. 4. As is obvious, the peak potentials are strongly pH dependent. The observed shift of the anodic and cathodic peaks towards more negative potentials by increasing the solution pH is due to the pH dependency of the electrode process. However, as is expected, the peak-to-peak separation, ΔE_p , remains almost constant during the displacement of peaks. Moreover, the influence of the pH on the rate constant of the electrochemical process is known for quinone derivatives, though this dependence is usually more complicated and non-monotonic [56]. It is noteworthy that, parallel to the shift in the peak potentials toward more negative values by increasing the solution pH, the peak currents also considerably increase.

The half-wave potentials, $E_{1/2}$, calculated as the average of the anodic and cathodic peak potentials of the corresponding cyclic voltammograms ($E_{pa} + E_{pc}$)/2 [57], were plotted against the solution pH. A sample $E_{1/2}$ -pH plot is shown in Fig. 5. In the case of all carbon paste electrodes containing anthraquinones AQ₁–AQ₅, the resulting plots consisted of three distinct linear portions with different slopes: –90 mV at low pH values of about < 4, –58 mV at intermediate pH values of about 4–10 and –28 mV at high pH values of about > 10 per unit of pH (see Fig. 5). The resulting $E_{1/2}$ -pH diagrams clearly indicate the formation of four different forms of the amino-anthraquinones used at the surface of the CPEs: the oxidized form AQNH₂ and its three reduced forms H₂AQNH₃⁺, H₂AQNH₂, and HAQNH₂⁻. The electrode surface reaction occurring at pH < 4 is a two-electron three-proton process involving the reduction of 9,10-

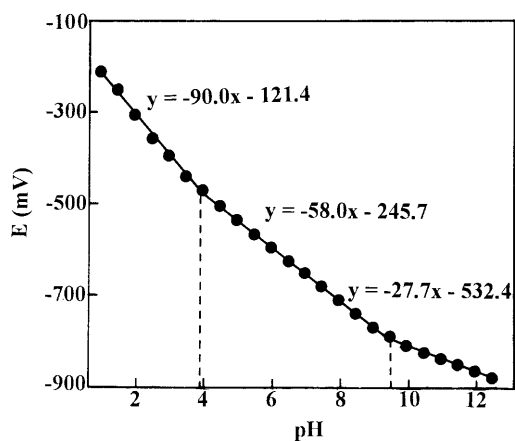
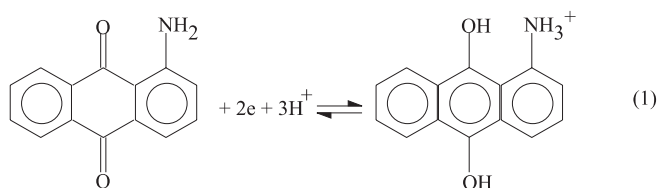
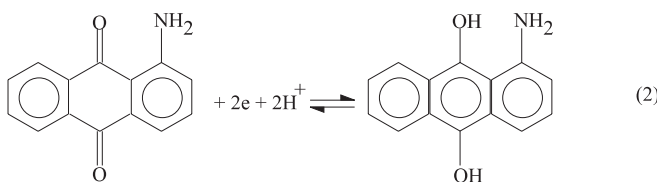


Fig. 5 pH-potential diagram for the CPE spiked with AQ₁

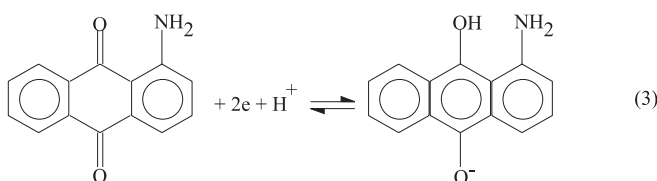
anthraquinone base to 9,10-anthracenediol and protonation of the substituted amino group as:



At the pH range of about 4–10, the anthraquinone derivatives undergo a two-electron two-proton process, producing the corresponding 9,10-anthracenediol compounds:



Finally, the electrode surface reaction at pH > 10 is a two-electron one-proton process resulting in an HAQ⁻ anion:

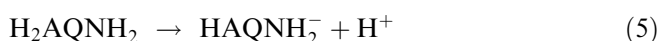
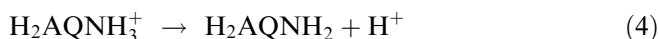


The values of formal potentials, E'_a , for all possible equilibria between the oxidized and reduced forms of anthraquinones AQ₁–AQ₅ (i.e. Eqs. 1–3) were calculated from the intercepts of the linear segments of the corresponding $E_{1/2}$ -pH plots and the results are given in Table 1. The uncertainties reported were estimated by a common reported method [58]. The apparent acidity constants for the protonated form of the anthraquinone derivatives used (Eqs. 4 and 5) were also evaluated from the change in slopes of the linear segment of the

Table 1 Formal potentials (E°) and pK'_a values for different redox and acid-base couples involved

Anthraquinone	Reaction	E° (mV/Ag, AgCl)	pK'_a
AQ ₁	(1)	-97 ± 6	–
	(2)	-172 ± 4	–
	(3)	-454 ± 5	–
	(4)	–	3.60
	(5)	–	8.83
AQ ₂	(1)	-67 ± 5	–
	(2)	-130 ± 4	–
	(3)	-423 ± 6	–
	(4)	–	3.76
	(5)	–	9.03
AQ ₃	(1)	-121 ± 4	–
	(2)	-246 ± 9	–
	(3)	-532 ± 7	–
	(4)	–	3.86
	(5)	–	9.58
AQ ₄	(1)	-138 ± 6	–
	(2)	-235 ± 7	–
	(3)	-530 ± 7	–
	(4)	–	3.85
	(5)	–	9.57
AQ ₅	(1)	-138 ± 4	–
	(2)	-287 ± 2	–
	(3)	-524 ± 6	–
	(4)	–	3.82
	(5)	–	9.70

$E_{1/2}$ -pH plots and the results are also included in Table 1.



As expected, both the E'_a and pK'_a values are strongly dependent on the nature of the conjugated forms studied as well as on the nature of substituents on the 9,10-anthraquinone structure. In order to further investigate the influence of 9,10-anthraquinone substituents on the electrochemical properties, the $E_{1/2}$ values were evaluated at a pH of 6, at which all anthraquinones used are reduced in a two-electron two-proton process. The resulting $E_{1/2}$ values are summarized in Table 2.

It is well known that the anthraquinones' structural parameters such as the inductive effect, mesomeric (hyperconjugation) effect, and steric hindrance of the side arms may influence the acid-base [47–49, 59] and electrochemical properties of anthraquinone derivatives [35–41]. Table 2 shows that the reduction of 1-amino-9,10-

Table 2 Values of the half-wave potentials ($E_{1/2}$) of the carbon paste electrodes spiked with different amino-anthraquinone derivatives at pH = 6

Anthraquinone	$E_{1/2}$ (mV/Ag, AgCl) (± 5)
AQ ₁	-560
AQ ₂	-520
AQ ₃	-590
AQ ₄	-615
AQ ₅	-620

anthraquinone occurs at a more negative potential (40 mV) in comparison with the 2-amino derivative. This is most probably due to the possible intramolecular H-bonding between the $-NH_2$ and $-CO-$ groups of the former ligand, which may stabilize the anthraquinonid form and may thus be partly responsible for the negative shift of $E_{1/2}$ [60]. On the other hand, the substitution of alkyl groups on different positions of 1-amino-9,10-anthraquinone will result in a relatively large shift of 30–60 mV towards more negative reduction potentials, most probably due to the increased donicity of the aromatic system.

The CPEs containing anthraquinone derivatives AQ₁–AQ₅ were found to be quite stable in acidic solutions. As an example, the cyclic voltammograms of one of the modified CPEs recorded in 0.5 M H₂SO₄ under increasing number of cycles are shown in Fig. 6. However, the electrodes begin to decompose in alkaline solutions. This is probably due to deprotonation of the anthraquinone derivatives at high pH values [47–49], which results in substantial release of the ligands from the carbon paste into the surrounding aqueous solutions.

A more satisfactory transport analysis for the modified CPEs can be afforded by chronoamperometry, as was illustrated previously [6, 61]. Analysis of the chronoamperometric behavior of porphyrin-containing carbon pastes by Takeuchi and Murray [6] revealed a short-time linear/semi-infinite diffusion response, showing a finite diffusion depletion of reactant at the carbon paste-water interface. Ravichandran and Baldwin [61]

also reported a diffusional process in a short chronoamperometric electroanalysis time for a carbon paste containing tetramethylphenylenediamine. Thus, in this work, the amperometric behavior of the CPEs containing compounds AQ₁–AQ₅ was examined in the absence of dioxygen. A sample current-time curve for the CPE spiked with AQ₄ is shown in Fig. 7A. A similar behavior was observed for other modified CPEs tested. The corresponding plot of current vs. $t^{-1/2}$ (Fig. 7B) reveals a straight line which extrapolates close to the origin.

The oxidized and reduced forms of the anthraquinone derivatives are known to be insoluble in water and the bulk solution contains no reduced anthraquinone. Thus, this type of near Cottrellian behavior is not due to a linear semi-infinite diffusion process, but it may be caused by the occurrence of finite diffusion in a thin film over a short time period [61]. By assuming diffusion controlled behavior for transfer of charge at the CPEs spiked with anthraquinone derivatives and using the potential step chronoamperometric experiments, the diffusion coefficients of compounds AQ₁–AQ₅ to the paraffin oil can be estimated [55]. According to the Cottrell equation (Eq. 6), the slope of the linear region of the I vs. $t^{-1/2}$ plot provides $D^{1/2}$ if other parameters are known. It should be noted that A was taken as the cross-sectional area of the disk electrode ($A = 0.05 \text{ cm}^2$).

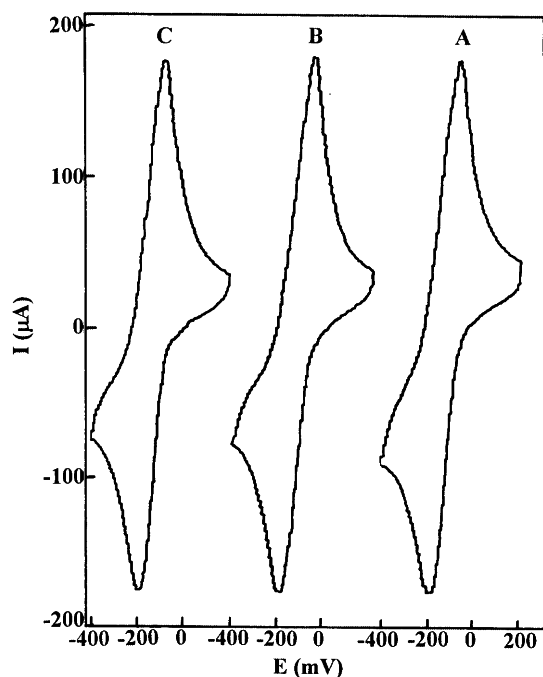


Fig. 6 Cyclic voltammograms of the CPE spiked with AQ₃ in a 0.5 M H₂SO₄ solution: **A** first scan, **B** after 25 cycles, and **C** after 50 cycles. Scan rate is 100 mV s⁻¹

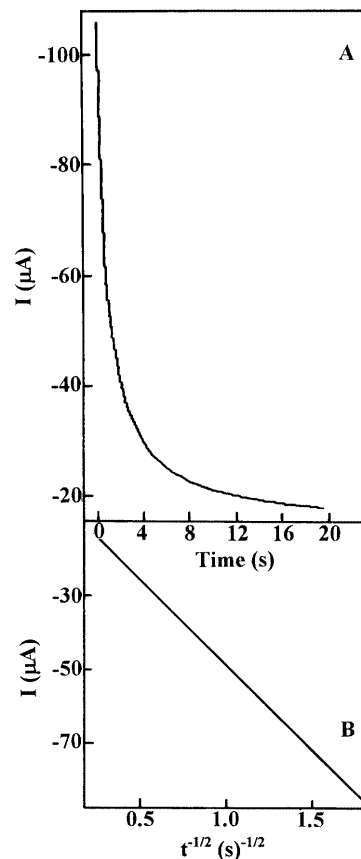


Fig. 7A Chronoamperogram obtained by the potential step technique at a potential of -400 mV in a 0.5 M H₂SO₄ solution for the CPE spiked with AQ₃. **B** The resulting I vs. $t^{-1/2}$ plot

Table 3 Diffusion coefficients for different amino-anthraquinone derivatives in paraffin oil

Anthraquinone	$10^8 D$ (cm ² /s)		$10^5 D$ (cm ² /s) in CH ₃ CN
	Collrell	Eyring	
AQ ₁	4.08	3.30	1.20
AQ ₂	4.21	3.63	1.32
AQ ₃	3.47	3.24	1.18
AQ ₄	3.69	3.38	1.22
AQ ₅	3.98	3.71	1.34

$$I = \frac{nFAD^{1/2}C_{AQ}}{\pi^{1/2}t^{1/2}} \quad (6)$$

The diffusion coefficients D evaluated from such linear plots are given in Table 3. An estimate of D values for diffusion coefficient of AQ₁–AQ₅ in paraffin oil was obtained by measuring it electrochemically in acetonitrile (Table 3) and relating the result to paraffin using a result from Eyring rate theory [62]: $D_1\eta_1 = D_2\eta_2$, where η is the viscosity. The D values estimated by this method are also included in Table 3. Comparison of the D values obtained by the two methods revealed that the estimated effective area of the CPE is larger than the cross-sectional area of the disk of electrode paste exposed to the solution by an average factor of about 1.1. Similar results have been reported for other modified CPEs [6, 26].

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