비양자성 매개물에서 (2, 4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine의 전기화학적 반응

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Electrochemical Behaviour of (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine in Aprotic Media

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요 약. (2, 4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine의 전기화학적 환원에 대하여 실온에서 순환전압전류 기술을 사용한 유리탄소전극(GCE)에서 N,N-dimethylformamide 하에서 0.1 M tetrabutylammoniumbromide로 조사하였다. 이민의 환원은 각각 한 전자를 포함하면서 2단계의 성공적인 단계로 일어난다. 이 매개물에서 처음 피크는 유리탄소전극 표면에서 약 -0.793 V(vs Ag/Ag$^+$)로 관측되었다. 그리고 그것은 더욱 안정하고 2번째 피크와 비교하여 명확하게 설명된다. 연구된 용매 매개물에서 이민의 확산계수(D_0)는 수정된 Randles-Sevcik 식을 이용해 계산되었다. 반응 종들의 전자 이동 계수(α) 또한 계산되었다.

주제어: (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine, 유리탄소전극(GCE), 확산 계수 (D_0), Randles-Sevcik 식

ABSTRACT. The electrochemical reduction of (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine was investigated in 0.1 M tetrabutylammoniumbromide in N,N-dimethylformamide at glassy carbon electrode (GCE) using the technique of cyclic voltammetry at the room temperature (290 K). The reduction of imines occurs in two successive steps, involving one electron in each. In this medium the first peak was observed at about -0.793 V (vs Ag/Ag$^+$) at the glassy carbon electrode surface, which is more stable and well defined as compared to the second peak. The diffusion coefficient (D_0) of imine in the investigated solvent media has been calculated using the modified Randles-Sevcik equation. The electron transfer coefficient (α) of the reactant species has also been calculated.

Keywords: (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine, Glassy carbon electrode (GCE), Diffusion coefficient (D_0), Randles-Sevcik equation

INTRODUCTION

Chemists seek selectivity and specificity in chemical reactions. Selective reductions are difficult and their success depends on the reducing agent. The imines are reduced by electrolysis without difficulty, and some articles have indicated that the amines are the products of the reduction of imines in either protic or aprotic solvents.[1-2]

Interest in the electrochemical reduction of imines began with the study of the polarographic behaviour of some ketones which get reduced at a high negative potential. Such ketones could be easily transformed to the corresponding imines, whose reduction occurs at a moderately negative potential.

The electrochemical behaviour of imines has been extensively studied by polarography in both aqueous and nonaqueous solutions. Under aqueous conditions reduction has been shown to consist of a two-electron, two-proton transfer which converts the >C=N linkage to a -CHNH$_2$ group. In keeping with this, the half-wave potential of the first reduction wave shows a pronounced dependence on pH (ranging between 2 to 4). Such studies are complicated, however, due to the hydrolysis of the azomethine compound into its constituent amine and carbonyl compound.[3-6]

While hydrolysis is not a problem when electrochemical studies are carried out in nonaqueous solvents, the results of such studies have shown the possibility of a number of electrochemical mechanisms. Thus, the two reduction waves seen in dimethylformamide (DMF) were

attributed by Scott and Jura[7] to two one-electron transfers followed by irreversible protonation of the dianion thus formed.

Remarkably, Bezuglyi *et al*. concluded that the first reduction wave in azomethine compounds in DMF involves an irreversible two-electron transfer, though both of these and the former researchers used diffusion current constants and the Nernstian slope to reach their differing conclusions.

The results of single sweep voltammetry studies, however, indicate that the reduction of imines in aprotic media proceeds via reversible one-electron transfer followed by an irreversible one-electron transfer and chemical reaction, in agreement with Scott and Jura.[8-9] Cyclic voltammetry was used by Andrieux and Saveants to study the reduction of several imines in both DMF and acetonitrile (AN). Depending on the solvent and the compound, it was possible to observe either a two-electron wave leading to the saturated amine or two one-electron waves associated with dimerization. In either case the reduction is irreversible. Studies by Fry and Reed[10] on several imines in DMF indicated that reduction of these compounds occurs by way of an irreversible two-electron transfer. It was postulated on the basis of polarography and cyclic voltammetry that the overall two-electron reduction in fact consists of a one electron transfer followed by rapid proton transfer and a second rapid electron transfer.[11-13]

Encouraged by these facts and non availability of report on the electrochemical behaviour of imine compounds obtained by condensation of 2-Phenyl-1H-quinolin-4-one and aromatic amine 2,4-Difluoro-phenylamine till date, in present work, first a new Schiff base of 2-Phenyl-1H-quinolin-4-one with 2,4-Difluoro-phenylamine are synthesized and secondly their electrochemical behaviour on glassy carbon electrode is examined. Kinetic parameters i.e. electron-transfer coefficient (α) of the electrode reaction and the diffusion coefficient (D_0) have also been calculated.

Experimental Study

Reagents

All the reagents used were of analytical grade. 2-phenyl-1H-quinolin-4-one was prepared according to reported method.[14] Stock solution of imine (Q=NAr) were prepared at a concentration of 1×10^{-3} M in DMF. The supporting electrolyte of tetrabutylammonium bromide (TBAB) was purchased from SISCO Research laboratories Pvt. Ltd., and used without further purification.

Synthesis of (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine (Q=NAr)

Imine (Q=NAr) was prepared as per mentioned in literature.[15] The general synthetic approach involved condensation of an equimolar mixture of corresponding 2-phenyl-1H-quinolin-4-one (0.01 mol) and 2,4-Difluoro-phenylamine (0.01 mol) in absolute ethanol in the presence of 2, 3-drops of glacial acetic acid for 3-4 hours. On cooling, flakes separated out which were filtered and recrystallised by the help of hot ethanol to give shining bright coloured needles of (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine (Q=NAr) in 70-80% yield (*Scheme* 1). Synthesized compounds were characterized by their IR and ^{1}H NMR studies. Formation of imine was indicated by the disappearance of one CO frequency of the quinolone moiety and free primary amino frequency of 2,4-Difluoro-phenylamine in the IR spectra. Also in ^{1}H NMR spectra, signals due to NH$_2$ were absent and characteristic signals were observed at δ 12.08 ppm (quinoline NH) (*Scheme* 1).

2-Phenyl-1*H*-quinolin-4-one   2,4-Difluoro-phenylamine   (2,4-Difluoro-phenyl)-(2-phenyl-1*H*-quinolin-4-ylidene)-amine
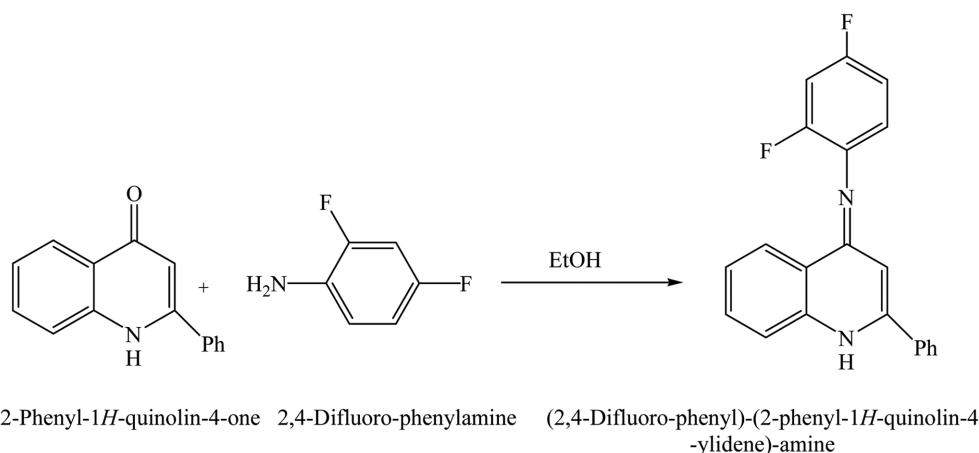
***Scheme* 1.**

Apparatus

The voltammetric measurements were carried out on an electrochemical analyzer (CH Instruments, USA, Model CHI 1230), equipped with a 10ml single compartment three-electrode glass cell. These systems were connected to a processor. All experiments were carried out in three-electrode system. Glassy carbon electrode (Part No.CHI 104) was used as the working electrode, a platinum wire as counter electrode and Ag/AgCl electrode as reference electrode. All solution used in the voltammetric system were deaerated with nitrogen for at least 15 min before executing the voltammetric experiments. All experiments were carried out at room temperature of 25 ± 1 ℃. The GCE was polished using 0.3 micron Al_2O_3 before each experiment.

Sample preparation

000.1 M stock solution of depolarizer i.e. (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine was prepared by dissolving accurately weighed amount in purified DMF owing to low solubility of imine in water. More dilute solutions were prepared from the stock solution with supporting electrolyte *viz.* 0.1 M Tetrabutylammoniumbromide (TBAB) solution in DMF just prior to analysis. The electrochemical measurements were then carried out.

Controlled potential electrolysis

Controlled-potential preparative electrolysis was carried out using H type cell separating the anode and cathode compartment by fine glass sinter. Other components of the cell assembly were as follows:

Cathode: Glassy Carbon Electrode
Catholyte: DMF + TBAB + (Q=NAr) compound
Total volume of catholyte: 100 ml
Anode: Pt sheet
Anolyte: DMF + TBAB

All measurements were carried out at controlled ambient temperature of 290K. A magnetic stirrer was used for agitation. CPE experiment was carried out at potential of about 200 mV more negative than that obtained in CV experiment. The Ag/AgCl electrode which is used as a reference electrode was placed in the same compartment along with GCE. The electrolysis was carried out for 12 hrs for complete reduction of (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine (Q=NAr). Reduction product was isolated and separated in column. To isolate the electrolysis product, DMF was distilled off in vacuo, the residue was shaken with dry ether and the supporting electrolyte was filtered off. The ethereal layer was

evaporated and the residue thus obtained was purified by column chromatography on silica gel using ethyl acetate and hexane (40:60 v/v) as eluent. The reduced product was identified as (2, 4-difluoro-phenyl)-(2-phenyl-1, 4-dihydroquinoline-4-yl)-amine by IR and NMR spectra.

Analysis by physico-chemical methods

Analysis of product had been carried out by usual physico-chemical methods. Reduction of (2, 4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine gives (2, 4-Difluoro-phenyl)-(2-phenyl-1, 4-dihydro-quinolin-4-yl)-amine (yield 76%). The product was characterized by C, H analyzer and spectrophotometric techniques (I.R. and N.M.R.).

The following observations were made:

1. A single clear spot on silica gel-G plate was obtained in iodine chamber, confirming that the product was a single compound and not a mixture.
2. The percentage of Carbon, Hydrogen and Nitrogen in the product was determined by PERKIN ELMER elemental analysis.
3. IR spectra were recorded in KBr on a SHIMADZU 400-50 infrared spectrophotometer (ν_{max} in cm^{-1}).
4. ^{1}H NMR spectra were recorded on JEOL AL 300 ^{1}H NMR spectrophotometer using $CDCl_3$ as solvent and TMS as an internal standard (chemical shift in δ ppm).

C, H, N, estimation value

The observed values of the carbon, Hydrogen and Nitrogen, in the product, were 75.23%, 4.65%, 8.51% respectively, as compared to the their theoretical values, which are 75.90%, 4.81%, 8.43% respectively, thus, confirming the product.

IR spectra

IR spectra of (2,4-Difluoro-phenyl)-(2-phenyl-1,4-dihydro-quinolin-4-yl)-amine is characterized by the disappearance of the (C=N) band in 1623-1641 cm^{-1} region in comparison with that obtained for the original compound. A sharp peak was observed at 3345 cm^{-1}, which shows reduction of imine group into amine group.

NMR spectra

^{1}H NMR spectrum (δ ppm): 12.1 (1H, br, NH), 6.1 (1H, s, H-3), 10.3 (1H, s, NH), 6.5-6.7 (4H, m, H-5, H-6, H-7 and H-8), 7.2-7.5 (5H, m, H-2', H-3', H-4', H-5' and H-6'), 6.2 (1H, s, H-3''), 6.4 (2H, q, H-5''and H-6'').

RESULTS AND DISCUSSION

Cyclic Voltammetric Investigation

The reduction of (2, 4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine (Q=NAr) at a GCE was studied by cyclic voltammetry (CV) in 0.1 M TBAB as supporting electrolyte in DMF. In the studied potential range, the reduction peak for DMF was not observed. The cyclic voltammogram obtained for 1×10^{-3} M imine (Q=NAr) solution (*Fig.* 1) shows two well defined irreversible waves. The reversal peaks of the two waves are almost nonexistent, indicating that the two waves correspond to two slow one electron transfers or a fast one electron transfer coupled with a rapid chemical reaction.

The study of effect of scan rate is made in order to postulate the mechanism and the feasibility of electrochemical reactions involved at GCE in this medium. The relationship between the peak current (i_p) and the voltage scan rate (v) is described by the modified Randles-Sevcik[16] equation:

$$i_p = (2.99 \times 10^5) \, n \, (\alpha n_a)^{1/2} \, A \, C \, D_0^{1/2} \, v^{1/2}$$

where, i_p is the peak current, α is the charge-transfer coefficient, n is the number of electron equivalents exchanged during the oxidation/reduction reversible process (electron stiochiometry), A is the active surface area of working electrode (cm^2), D_0 the diffusion coefficient (cm^2 s^{-1}), C is the bulk concentration of the diffusing species (mol cm^{-3}), v is the voltage scan rate (Vs^{-1}), F is the faraday constant, R is the gas constant, and T is the absolute temperature (K).

In the present study, the cathodic peak current (i_{pc}) was plotted against the square root of the scan rate ($v^{1/2}$) in
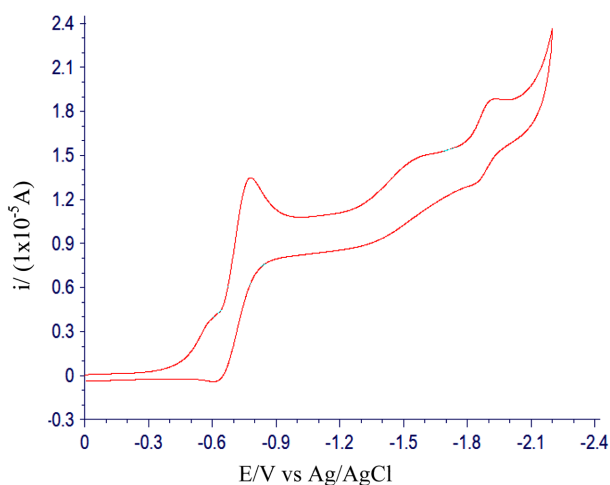

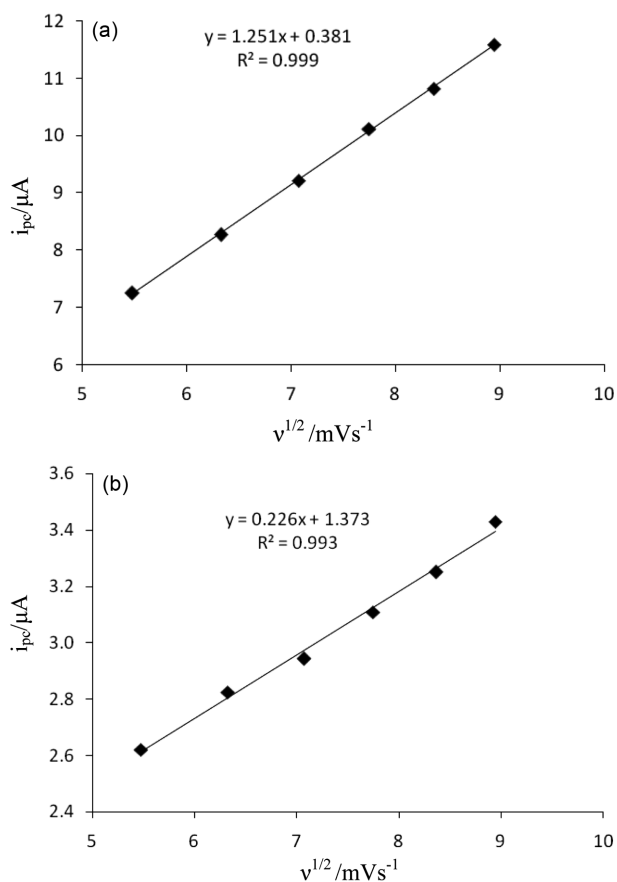**Fig. 1.** Cyclic voltammogram of 1×10^{-3} M Q=NAr at GC electrode.

Fig. 2. (a) Plot of cathodic peak current as a function of $v^{1/2}$ (Ist wave). (b) Plot of cathodic peak current as a function of $v^{1/2}$ (IInd wave).

order to apply the Nicholson-Shain criteria to elucidate the reaction mechanism. The cathodic peak current (i_{pc}) of two waves were found in correlation with the square root of the scan rate ($v^{1/2}$), with correlation coefficients of 0.999 and 0.993 for first and second waves, respectively (*Fig.* 2a, 2b). Nicholson-Shain criteria state that the linear change of the current with the scan rate is an indication that the process is diffusion-controlled.[17,18] But there appeared a non zero intercept, which may be due to the electron transfer process complicated by the associated adsorption. A number of electrochemical criteria are applied to establish the nature of the two waves.
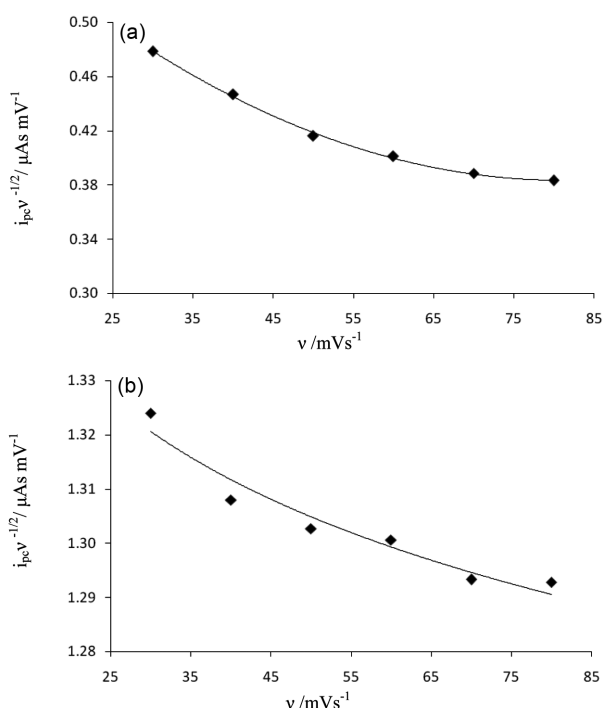
The widths of the first cyclic voltammetric waves (E_{pc}-$E_{pc}/2$) at different scan rates are observed to be insignificantly greater than the theoretical value expected for a reversible charge-transfer step (*Table* 1). The peak potential, E_{pc}, does shift in a negative direction with increasing scan rates. The plot of E_{pc} vs. $\log v$ yields a straight line. The variation of current function, ($i_{pc} / v^{1/2}$), with scan rate v is an important diagnostic criterion for establishing the

Table 1. First wave characteristics for (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine in 0.1 M TBAB/DMF at 290 K

Scan rate (mVs^{-1})	$-E_{pc}$ (V)	i_{pc} (μA)	$E_{pc} - E_{pc}/2$ (mV)	$i_{pc}/\nu^{1/2}$ ($\nu As\ mV^{-1}$)
30	0.780	7.256	69	1.3240
40	0.787	8.272	70	1.3080
50	0.793	9.215	67	1.3027
60	0.799	10.12	65	1.3066
70	0.802	10.82	63	1.2933
80	0.807	11.59	66	1.2928

Table 2. Second wave characteristics for (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine in 0.1 M TBAB/DMF at 290 K

Scan rate (mVs^{-1})	$-E_{pc}$ (V)	i_{pc} (μA)	$E_{pc} - E_{pc}/2$ (mV)	$i_{pc}/\nu^{1/2}$ ($\nu As\ mV^{-1}$)
30	1.921	2.621	70	0.4785
40	1.925	2.825	68	0.4467
50	1.928	2.943	66	0.4162
60	1.930	3.108	73	0.4012
70	1.934	3.251	66	0.3885
80	1.936	3.429	67	0.3833

Fig. 3. (a) Plot of $i_{pc}/\nu^{1/2}$ vs logν for 1×10^{-3} M Q=NAr 1 mM at GC electrode (I^{st} wave). (b) Plot of $i_{pc}/\nu^{1/2}$ vs logν for 1×10^{-3} M Q=NAr at GC electrode (IInd wave).

type of mechanism by cyclic voltammetry. The current function of this cathodic peak, $i_{pc}/\nu^{1/2}$, decreases slightly with scan rate (*Fig.* 3a). According to these results the underlying process is expected to be an irreversible one electron transfer followed by chemical reaction. This reaction could be regarded as a protonation of the imine radical anion [QNAr]$^{.-}$.

The cyclic voltammetric results in the study of the second wave are shown in *Table* 2. It can be seen that (E_{pc}-$E_{pc}/2$) and E_{pc} shift towards more negative potential with increasing scan rates. The second reduction wave which corresponds to the addition of one electron to the radical

[QNHAr]$^{.}$, leading to the formation of the anion [QNHAr]$^{-}$, was found to be electrochemically irreversible, with no anodic reversal current associated with it. The plot of the cathodic peak current (i_{pc}) against the square root of the scan rate ($\nu^{1/2}$), and the current function ($i_{pc}/\nu^{1/2}$) values plotted against the scan rate are given in *Fig.* 2(b) and *Fig* 3(b) respectively. Furthermore, linear change of the current with the square root of scan rate and the ratio $i_{pc}/\nu^{1/2}$ decreases on increasing the scan rate. All the above evidences suggest that the irreversibility of the second wave is due to a moderately fast first-order reaction involving the product of the second electron-transfer.

Estimation of αn_a and diffusion coefficient D_0

The cathodic peak potential (E_{pc}) of the reduction peak was dependent on scan rate. The shift of peak potential was observed towards more negative values with the increase in scan rates which indicates a diffusion controlled irreversible nature of the system,[19] where the peak potential is given by,

$$E_p = E^0 - (RT/\alpha\ n_aF)\ [0.78 - \ln(k^0/D_0^{1/2}) + \ln(\alpha\ n_aF\nu/RT)^{1/2}]$$

where α is the cathodic charge transfer coefficient, n_a is the number of electrons involved in the rate determining step, D_0 the diffusion coefficient and k^0 is the standard rate constant of the electrochemical reaction. In the present work, the plot of E_{pc} vs. logν was linear having a correlation coefficient of 0.996 and 0.985 for I^{st} and IInd peak respectively (*Fig.* 4(a), 4(b)) and this behaviour was consistent with the EC nature of the reaction in which the electrode reaction is coupled with an irreversible follow-up chemical step.[20,21] The value of αn_a as calculated from the slope of the plot between E_{pc} and logν, is 0.472 and 0.701 for I^{st} and IInd peak respectively. In most of the irreversible cases, α lies in the range from 0.30 to 0.70, thus the number of electrons transferred in each reduction step is one.
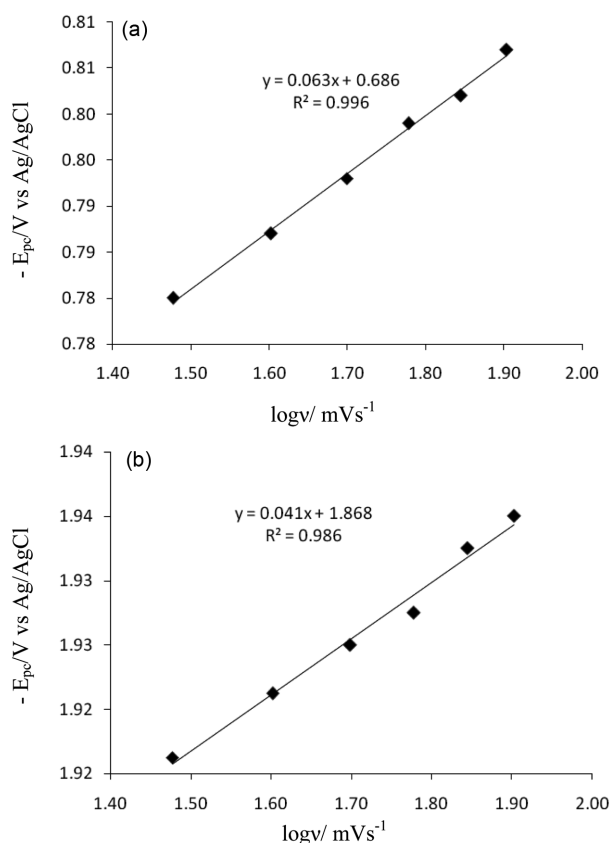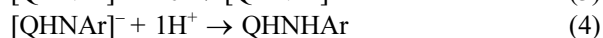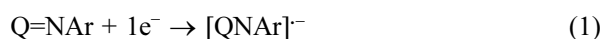
Fig. 4. (a) Plot of E_{pc} vs logv for 1×10^{-3} imine (Q=NAr) (I[st] wave). (b) Plot of E_{pc} vs logv for 1×10^{-3} imine (Q=NAr) (IInd wave).

The D_0 values for Q=NAr can be determined from the slope of i_{pc} vs $v^{1/2}$ plot, after careful substitution and unit analysis. The values of diffusion coefficients (D_0) are found to be 1.02×10^{-3} cm^{2}s^{-1} and 4.37×10^{-2} cm^{2}s^{-1} for I[st] and IInd peak respectively.

Electrode reaction pathway

In this study on the electrochemical reduction of imines in dimethylformamide media, irreversible two electron reduction waves were observed with cyclic voltammetry at moderate to slow sweep rates. This has been attributed to a rapid ECEC type reaction whereby the substrate imine picks up two electrons and two protons and is converted to the saturated amine, as shown below:

$$Q=NAr + 1e^- \rightarrow [QNAr]^{\cdot-} \qquad (1)$$
$$[QNAr]^{\cdot-} + 1H^+ \rightarrow [QHNAr]^{\cdot} \qquad (2)$$
$$[QHNAr]^{\cdot} + 1e \rightarrow [QHNAr]^- \qquad (3)$$
$$[QHNAr]^- + 1H^+ \rightarrow QHNHAr \qquad (4)$$

The reaction is initiated by the electrode reduction of the imine to its radical anion (reaction 1). The radical anion

then picks up a proton from solvent impurities or by abstraction from either the solvent or electrolyte to produce a protonated radical (reaction 2). The reduction potential for the protonated radical is less negative than that for the imine, so it is immediately reduced to a protonated anion (reaction 3). Subsequent protonation then gives the saturated amine product (reaction 4).

CONCLUSION

The investigations have demonstrated that examined Q=NAr i.e. (2,4-difluoro-phenyl)-(2-phenyl-1H-quinolin-4-ylidene)-amine has two reduction peaks at GCE in DMF. On the basis of the results obtained, the postulated electrode reaction mechanism pathway for Q=NAr can conveniently be claimed as EC mechanism. The electrochemical reduction occurs through acceptance of two electrons by successive one electron peak followed by chemical reaction. In order to test the validity of the proposed mechanism controlled-potential preparative electrolysis was carried out at the potential 200 mV more than the potential of the second peak for Q=NAr and the reduction products were isolated and identified by spectroscopic methods.

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