Electrochemical Study of Some Substituted Chromene Derivatives in Nonaqueous Media at Pt, Au and Glassy Carbon Electrodes

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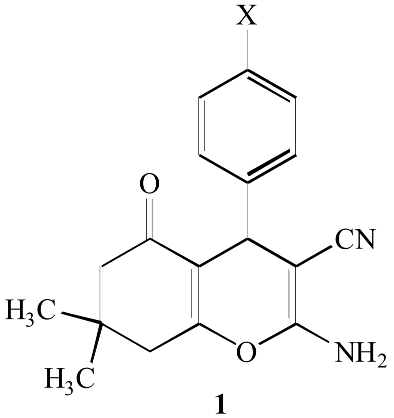
Abstract: The redox characteristics of some substituted chromene derivatives has been investigated in different nonaqueous solvents such as, 1,2- dichloroethane (DCE), dichloromethane (DCM) and acetonitrile (AN) using 0.1mol dm^{-3} tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at platinum, gold and glassy carbon electrodes, using cyclic voltammetry. Through controlled potential electrolysis (CPE), the product of oxidation and reduction can be separated and identified. The product of oxidation was found to be the corresponding bis-compound. On the other hand, the reduction occurs in a single two electron process to give the dianion, which abstracts protons to saturate the (-C=O) bond. The effect of substituents on the redox mode of an electroactive site has also been studied.

Keywords: Chromene, cyclic voltammetry, oxidation, reduction, non-aqueous solvent, platinum electrode, glassy carbon electrode, gold electrode.

1. INTRODUCTION

The electrochemistry of heterocyclic compounds with nitrogen heteroatom has been extensively studied [1-9]. In spite of great importance and wide uses of the heterocyclic aromatic compounds with oxygen or sulphur atoms, it is rare to find an attempt to study their electrochemical redox characteristics. For this reason, it was found worthwhile to review this work dealing with the electrochemical redox characteristics of some 4-substituted 2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromone-3-carbonitrile derivatives (**1a-e**).



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a, X = H
b, X = Br
c, X = Cl
d, X= OCH_3
e, X = NO_2

These compounds were extensively studied using cyclic voltammetry in dichloromethane (DCM), 1,2-Dichloroethane (DCE), and acetonitrile (AN) on platinum, gold and glassy-carbon electrodes. The number of electrons participating in each electrode process was determined using coulometric technique. Separation and identification of the final products of both oxidation and reduction process were made through the controlled potential electrolysis.

2. MATERIALS AND METHODOLOGY

The organic compounds were synthesized according to the procedures outlined in the literature [10]. All the synthesized compounds were purified by repeated crystallization. dried under reduced pressure and the purity was checked by thin layer chromatography.

Electrochemical measurements, including cyclic voltammetry, coulometry, and controlled potential electrolysis, were carried out using the following apparatus: The EG&G Princeton applied research model 283 Potentiostat/Galvanostat controlled from a PS-486-Dx microcomputer *via* a National Instrument IEEE-488 through GPIB board by means of M270/250 program was used for the electrochemical control.

All measurements were carried out with 2.5 x 10^{-4} mol of the reactant in 15 ml dry oxygen-free solvent with 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate as supporting electrolyte. Dichloromethane (DCM), 1,2-Dichloroethane (DCE), and acetonitrile (AN) were used as solvents. During the solvent purification, all the processes were performed under a dry oxygen-free argon atmosphere. Fractionation was carried out using a 120 cm column filled with glass spirals at a reflux ratio of 50:1. All the purified solvents were stored under argon in the dark. Purification of different solvents was carried out according to the literature [7,11,12].

Supporting electrolyte, tetra-*n*-butyl ammonium perchlorate (TBAP), was purified by consecutive crystallization from ethanol/water (9:1, v:v) and dried before use.

The working electrodes were Pt (0.00785 cm^2), glassy carbon (0.00785 cm^2) or Au (0.00375 cm^2) electrode, and the auxiliary electrode was Pt wire immersed in the corresponding electrolyte. The reference electrode was $Ag/AgCl/Cl^-$ (sat. AN) and the potential (E_P) values are referred to the redox potential of ferrocenium/ferrocene system [13].

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2.1. Controlled Potential Electrolysis (CPE)

CPE experiments were carried out in dry acetonitrile containing 0.1 mol.dm^{-3} tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. The potential was controlled at the current plateau of the oxidation or reduction peaks (300 mV, more positive or more negative than the E_P in oxidation and reduction processes, respectively). As a working electrode, a platinum gauze anode (*ca*. 80 cm^2) was used. The progress of the electrolysis was followed by periodically recording the decrease in peak current with time. From time to time, the working Pt gauze electrode was removed from the cell, sprayed with pure acetone and burned in a direct flame, cooled and replaced in the cell. After the completion of electrolysis, the cell was disconnected from the circuit and the solvent was evaporated in the vacuum. The residue was shaken with dry ether and the supporting electrolyte was filtered off. The ethereal layer was evaporated in turn. The obtained residue was chromatographed on thin layer silica gel plates using chloroform as an eluent. The main oxidation product of **1a** obtained was scraped off the plate and extracted with acetonitrile, filtered and evaporated in vacuum.

Oxidation Product of 1a

The resulting solid compound was identified as biscompound (m.p. 285°C), (yield 72%). Anal. Calcd: C, H, N. Found: C, H, N. The ^{1}H NMR (DMSO, TMS) spectrum of **1a**:– δ 7.95-7.85 (m, 2H, 2NH), 7.52-7.13 (m, 10H, Ar-H); 4.25-4.20 (m, 2H, 2CH), 2.76-2.62 (m, 4H, 2CH$_2$), 1.91-1.82 (m, 4H, 2CH$_2$), 1.14-1.10 (m, 12H, 4-CH$_3$) ppm. As shown from the results of ^{1}H NMR, the disappearance of the characteristic signal corresponding to NH$_2$ protons at δ= 6.90 ppm, whereas the appearance of two signals corresponding to two –NH protons at δ=7.95-7.85 ppm, which are lost after D$_2$O exchange. Mass spectrum: shows the main fragments at m/z 586, parent; 293 (M$^+$/2), 267 (M$^+$-CN), 215 (M$^+$-NC-C=C-NH$_2$), 138 (M$^+$ -C$_6$H$_5$), 110(-C=O), 68 (-C-(CH$_3$)2).

Reduction Product of 1a

The resulting solid has (m.p. 264°C), (yield 60%). Anal. Calcd: C,72.97; H,6.76; N, 9.46. Found: C,72.82; H,6.71; N,9.32; the IR spectrum (KBr) is characterized by the disappearance of the band 1680 cm^{-1} (C=O) in comparison with that obtained for the original compound **1a**. The ^{1}H NMR (DMSO, TMS) spectrum of **1a**:– δ= 11.1 (s, br, 1H, OH), 8.4 (s, 1H, CH), 7.52-7.13 (m, 5H, Ar-H); 6.9 (m, 2H, NH$_2$), 4.2 (s, 1H, CH), 2.75-2.6 (br, 2H, CH$_2$), 1.90-1.81 (br, 2H, CH$_2$), 1.14-1.10 (m, 6H, 2CH$_3$) ppm. As shown from the results of ^{1}H NMR, the appearance of the characteristic signals corresponding to the proton of the (OH) at δ=11.1. Mass spectrum: shows the main fragments at m/z 296; parent; 270 (M$^+$-CN); 218 (M$^+$-NC-C=C-NH$_2$); 141 (M$^+$ -C$_6$H$_5$); 113 (-C=O), 71 (-C-(CH$_3$)2).

3. RESULTS AND DISCUSSION

To study the effect of the substituents on the redox mode and the electrochemical characteristics of the investigated compounds **1a-e**, all measurements were carried out in dichloromethane (DCM), 1,2-Dichloroethane (DCE), and acetonitrile (AN) as solvents, using tetra-*n*-butyl ammonium perchlorate (TBAP) as a supporting electrolyte (0.1 mol.dm^{-3}), at 25°C at platinum, gold and glassy-carbon electrodes. The

Table 1. The Voltammetric Data of Compounds (1a-e)

Compd	Electrode	AN		DCE		DCM	
		D.N. 14.1		0.100		1.00	
		E_P^R	E_P^O	E_P^R	E_P^O	E_P^R	E_P^O
1a	Pt	-1620	1355	-2073	1593	-1878	1648
σ = 0	GC	-2215	1371	-2184	1593	-2200	1593
	Au	-2267	1787	-1716	1522	-2184	1537
1b	Pt	-1934	1426	-1740	1565	-1620	1569
σ = 0.23	GC	-2225	1371	-2227	1593	-2267	1648
	Au	-2040	1410	-1763	1521	-2240	1648
1c	Pt	-1823	1482	-1551	1604	-1668	1569
σ = 0.23	GC	-2185	1427	-2156	1565	-1958	1565
	Au	-2184	1482	-2045	1537	-2267	1593
1d	Pt	-1684	1371	-2017	1565	-1767	1565
σ =-0.27	GC	-2209	1366	-2165	1537	-2128	1537
	Au	-2203	1360	1906	1287	-1906	1565
1e*	Pt	-1782	940	-1716	1093	-1535	1055
σ = 0.78	GC	-1764	960	-1740	1117	-1459	1055
	Au	-1840	1226	-1716	998	-1763	1379

* There are another peaks with E_p =-1360 mV(AN); Ep=-1304 mV(DCE) and Ep=-1420 mV(DCM).

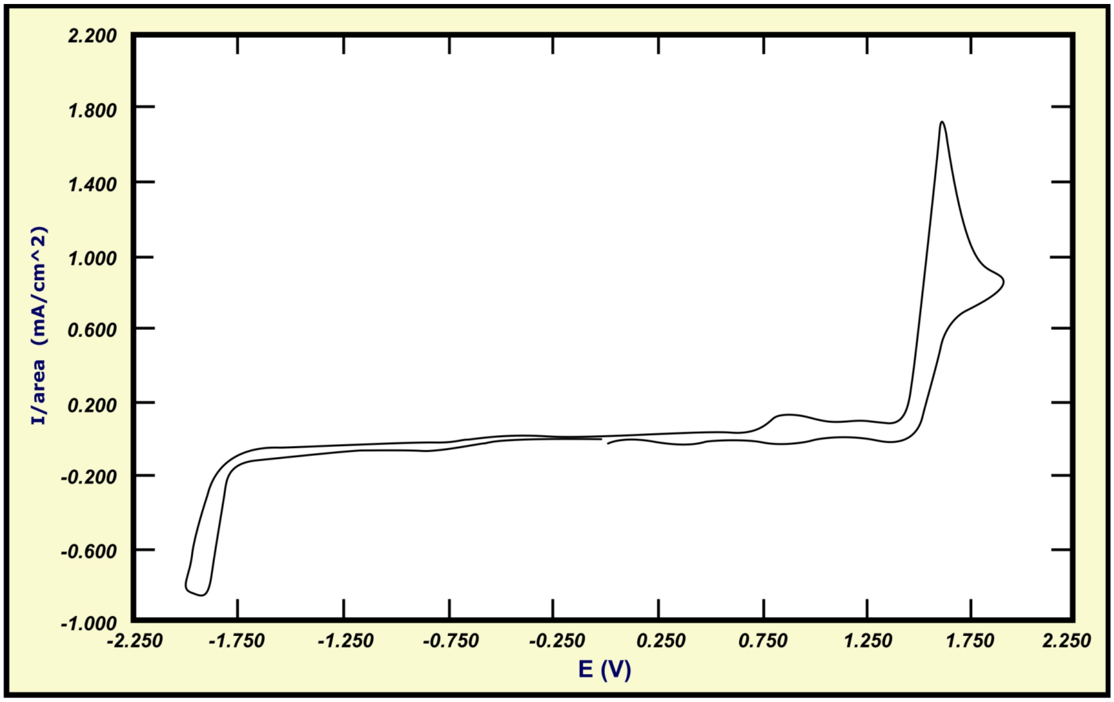


Fig. (1). Cyclic voltammogram of compound 1c in An at glassy carbon (GC) electrode (Scan rate = 100 mV/s; T = 25°C).

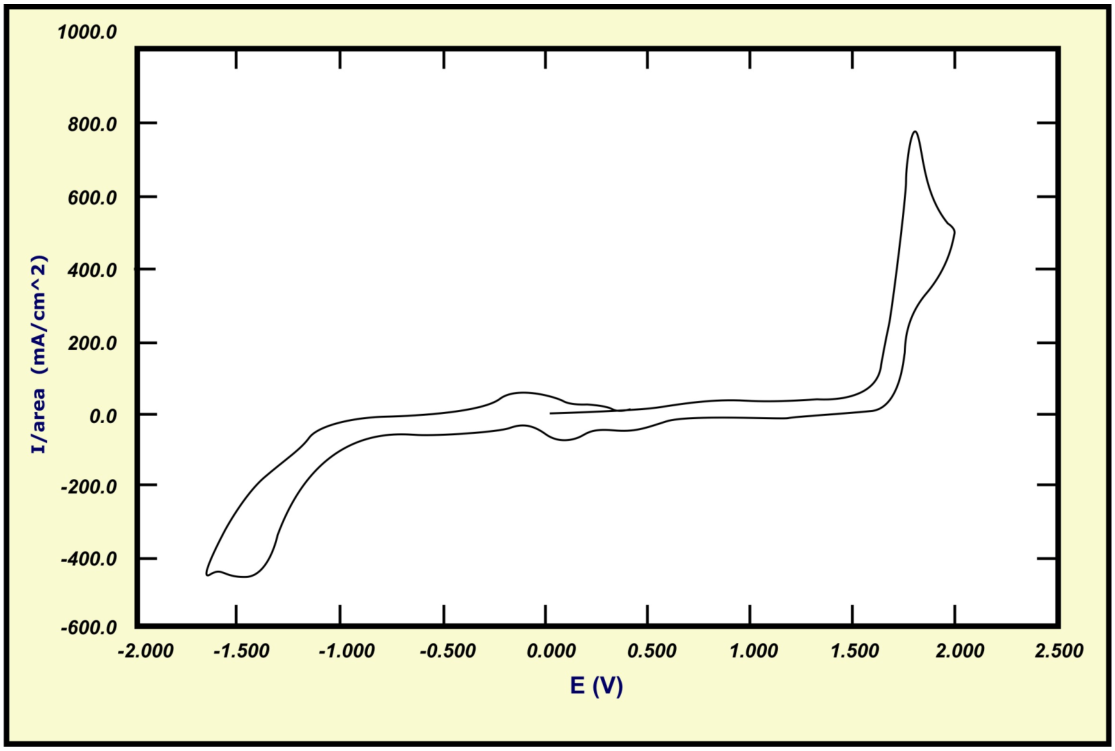
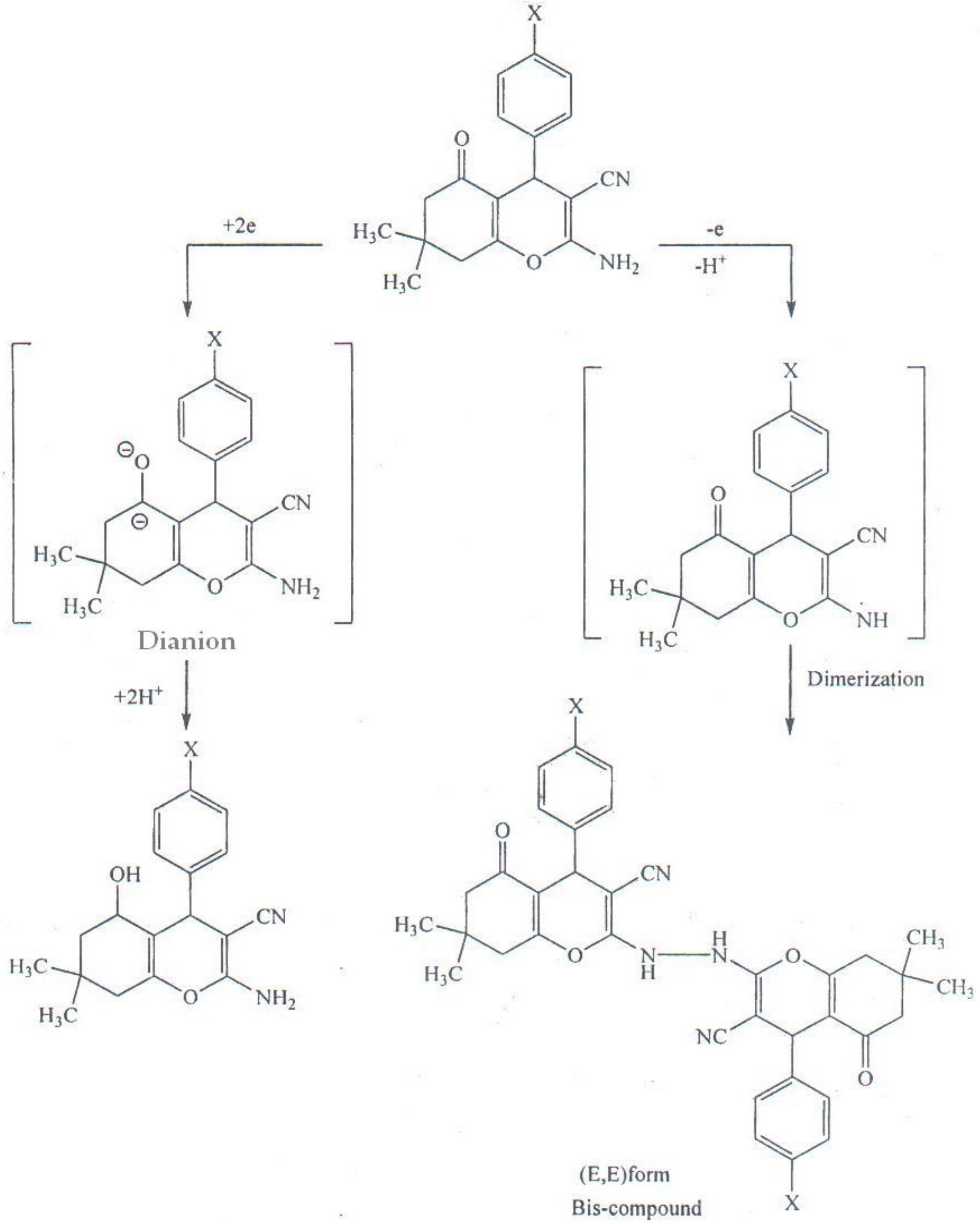


Fig. (2). Cyclic voltammogram of compound 1b in DCE at Pt-electrode (Scan rate = 100 mV/s; T = 25°C).

data are summarized in Table **1**. An example of the cyclic voltammograms of the investigated compounds is shown in Figs. (**1**, **2**).

From the data obtained in Table **1**, from the shape of the cyclic voltammograms, and also from the results of the coulometric measurements, and the isolation and identification of the controlled potential electrolysis products, it was evident that all compounds were oxidized in a single irreversible one electron process following the well known pattern of EC-mechanism at potential almost the same as that of the first oxidation wave of primary aromatic amine (-NH_2) [14]. They were oxidized through one electron loss to give the radical-cation, which lost one proton to give the corresponding (- NH) radical. The formed radical undergoes a dimerization reaction to give the (E-E) form of the bis- compound (Scheme **1**).



Scheme 1.

On the other hand, these compounds were reduced in a single irreversible two electron reduction process to give the dianion, which is a strong basic enough to abstract two protons from the media to saturate the (-C=O) bond [15-18]. Compound 1e displayed another second reduction wave, as well, which is characteristic for the reduction of the attached aromatic nitro group [19-21].

The effect of substituents on both oxidation and reduction of an electroactive site can be illustrated by applying the well-known modified Hammett equation (1) of the form [22-24].

$$E^*_P = \rho_x \sigma_x + E_P^H \qquad (1)$$

where, σ_x is the Hammett constant, ρ_x is the polarographic reduction or oxidation constant, and E^*_P, E_P^H are the peak potentials of the substituted and unsubstituted compounds, respectively. Fig. (**3**) illustrates Hammett equation correlations of the peak potentials **1a-e** for both oxidation and reduction processes.

It is obvious from the equations Table **2**, that the magnitude of both oxidation and reduction constants ρ_x^{Ox} and ρ_x^{Red} are almost the same. This indicates that the resonance interaction between the substituent and both reduction and oxidation centre in the molecule are almost equal.

All the investigated compounds behave similarly by using three monoaqueous solvents (DCM, DCE, and AN). A linear relation between ΔE_P and the doner number of the solvent [25] is obtained Fig. (**4**).

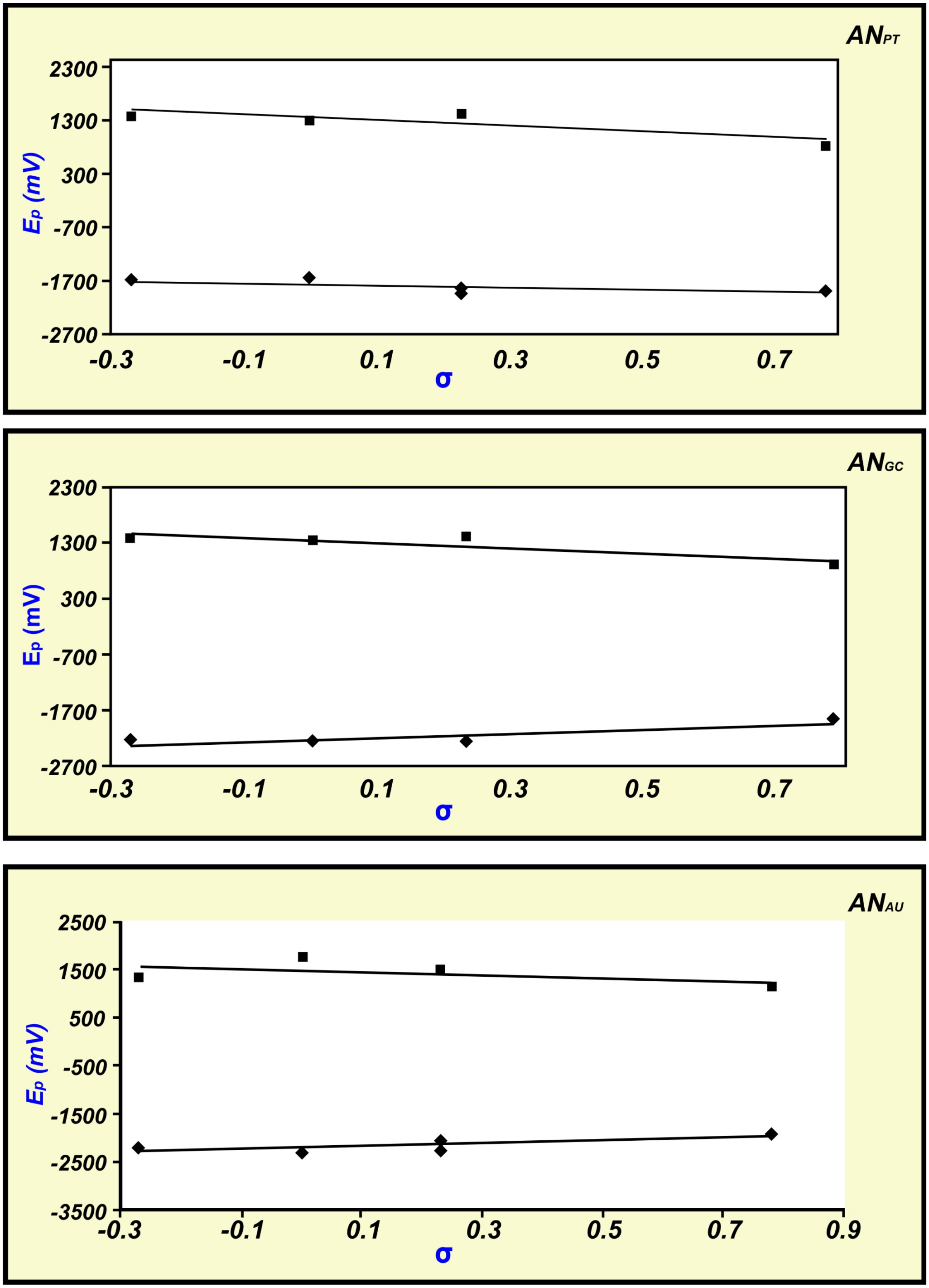


Fig. (3). Dependence of E_P^O and E_P^R of compounds (1a-e) in AN on Hammett substitution constant.(σ) at platinum, glassy carbon and gold electrodes.

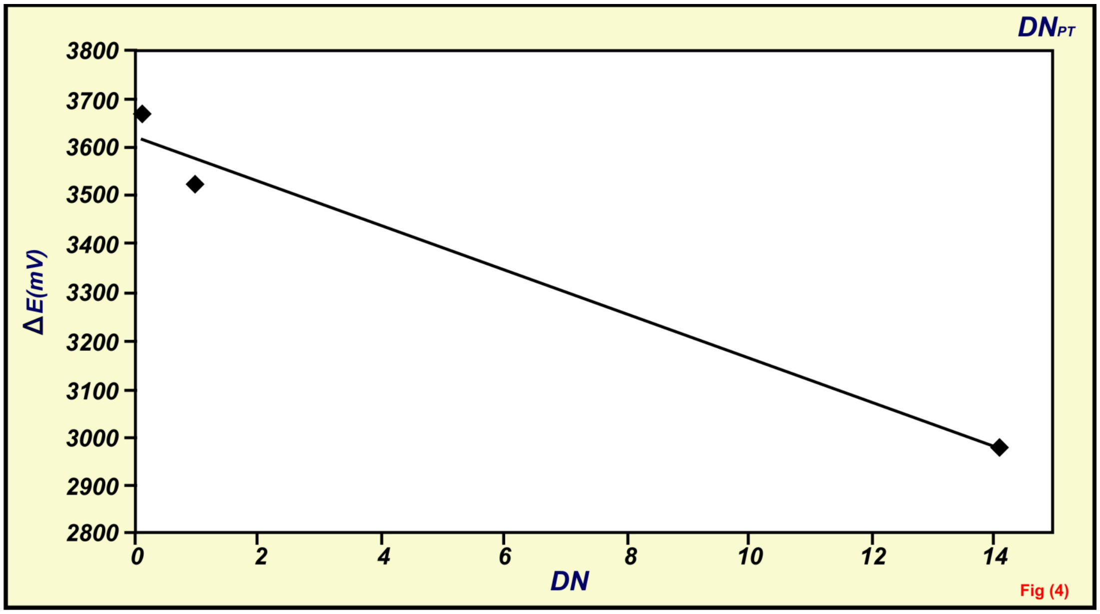


Fig. (4). Dependence of $\triangle E_p = (E_p^O - E_p^R)$ of compound 1a on the donor number (DN) of the solvents.

Table 2. Hammett Correlation of Compounds (1a-e) in DCM, DCE and AN

Solvent (WE)	σ – E_P(v) Plot equ.	
	Reduction	Oxidation
DCM (Pt)	$E_P^R = 0.277\,\sigma_x - 1.748$	$E_P^O = -0.542\,\sigma_x + 1.596$
DCM (GC)	$E_P^R = 0.68\,\sigma_x - 2.134$	$E_P^O = -0.481\,\sigma_x + 1.573$
DCM (Au)	$E_P^R = 0.188\,\sigma_x - 2.109$	$E_P^O = -0.166\,\sigma_x + 1.577$
DCE (Pt)	$E_P^R = 0.357\,\sigma_x - 1.889$	$E_P^O = -0.562\,\sigma_x + 1.574$
DCE (GC)	$E_P^R = 0.419\,\sigma_x - 2.176$	$E_P^O = -0.424\,\sigma_x + 1.563$
DCE (Au)	$E_P^R = 0.125\,\sigma_x - 1.853$	$E_P^O = -0.330\,\sigma_x + 1.437$
AN (Pt)	$E_P^R = 0.14\,\sigma_x - 1.741$	$E_P^O = -0.406\,\sigma_x + 1.394$
AN (GC)	$E_P^R = 0.438\,\sigma_x - 2.205$	$E_P^O = -0.395\,\sigma_x + 1.376$
AN (Au)	$E_P^R = 0.387\,\sigma_x - 2.182$	$E_P^O = -0.259\,\sigma_x + 1.503$

4. CONCLUSION

An electrochemical study, related to the redox characteristics of some substituted chromene 1a-e in nonaqueous solvents, has been performed using cyclic voltammetry. The redox mechanism is suggested and proved. All compounds are oxidized in a single irreversible one electron process following EC-mechanism to give a dimmer. They are reduced in a single irreversible two electrons step gives dianion, which abstract two protons from the media to saturate the (-C=O) bond.

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