Research Journal of Chemical Sciences ______ ISSN 2231-606X
Vol. **3(10),** 44-50, October **(2013)** *Res. J. Chem. Sci.*

Cyclic Voltammetric Studies of Synthesized Cardanol based Azo Dyes

Husnasarvari Maqbool, Shimoga D Ganesh, Umesh Chandra, Bghatta E Kumaraswamy and Vasantakumar K Pai
Dept. of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankarghatta-577451, Shimoga(D), Karnataka(S), INDIA

Available online at: www.isca.in, www.isca.me
Received 22nd August 2013, revised 31st August 2013, accepted 16th September 2013

Abstract

*The efficient method for the synthesis of ten cardanol azo dyes using aniline and its derivatives is described. Coupling reaction of cardanol affording high yield in slightly acidic media was observed. All the dyes were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, ultra violet - visible spectroscopy and mass spectrometry. The electrochemical behavior of these cardanol based azo dyes has been investigated by cyclic voltammetric technique by using sulfuric acid as supporting electrolyte. In addition, the effect of scan rate on dyes (**2a – 2j**) showed irreversible one step two electron diffusion controlled reduction process. The peak potential was found to shift in the cathodic direction with increase in scan rate indicating the irreversible nature of the electrode reaction.*

Keywords: Cardanol, CNSL, cyclic voltammetry (CV), marker, reduction, Azo dyes.

Introduction

The synthetic pathway in the production of fine chemicals from waste renewable natural organic raw materials is representative of the methodology used to make particular class of compounds. The purpose of this attractive topic of research is especially to recycle huge amounts of agro-industrial wastes *via* economically low cost feasible synthetic routes and to avoid expensive starting materials.

In this background, cardanol, obtained from Cashew Nut Shell Liquid (CNSL), a side product of the cashew industry, is the active constituent of CNSL, which is cheap, and renewable natural source considered as a starting material for the preparation of azo dyes because of its phenolic characteristics associated with polyketide unsaturated long chain.

CNSL is essentially a mixture of four phenolic compounds namely anacardic acid, cardol, cardanol and 2-methylcardol (figure 1); the vacuum distillation of cashew nut shell liquid finally affords cardanol. Cardanol, a mixture of *meta*-alkylphenols with variable degree of unsaturation attached to the benzene ring, is indeed a mixture of saturated (3-*n*-pentadecylphenol), monoolefinic [3-(n-pentadeca-8-enyl)phenol], diolefinic [3-(*n*-pentadeca-8,11-dienyl)phenol], and triolefinic [3-(*n*-pentadeca-8,11,14-trienyl)phenol]; remarkably in the mixture, both *E* and *Z* isomers are present, typically major ones are *Z* components.

Cardanol and its derivatives have innumerable applications in polymer based industries such as friction linings, paints, varnishes, laminating resins, rubber compounding resins, polyurethane based polymers, surfactants, epoxy resins and wood preservatives. Because of their unique properties, cardanol catches the attention of the scientists for their potential applications as resins[1], liquid crystalline polymers[2], biobased amphiphiles[3] and in organic synthesis[4] and several studies were also reported the introduction of cardanol into various macrocyclic frame works such as fullerene[5], phthalocyanine[6] and porphyrins[7-10].

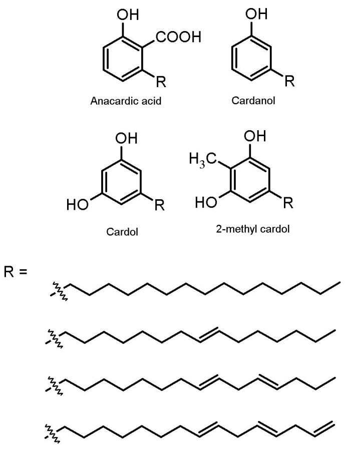


Figure-1
Components of CNSL

On the other hand, the rapid growth in the hi-tech uses of dyes, particularly in petroleum marker dyes[8] is beginning to make an impact. Although the volumes of hi-tech dyes will remain small in comparison to dyes for traditional applications, the worth will be significant because of the higher price of these specialized dyes.

For this reason, the marker dyes containing natural product such as cardanol and various aromatic amines were developed for their potential application as a diesel fluorescent marker[11]. Over the last few years scientists have interested to synthesize cardanol formaldehyde resins as an extended synthetic route from cardanol based azo dyes.

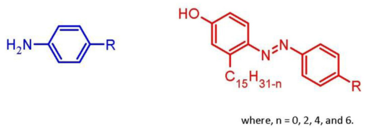
Considering all these factors, here we report the synthesis of cardanol based azo dyes using aniline and its derivatives. The limitations of existing methods for diazotization of cardanol involves strong alkaline conditions while coupling and the presence of electron-rich amino compounds for effective coupling in order to improve the yield becomes obvious in our attempts to prepare cardanol azo compounds in better yield.

Material and Methods

General: IR spectra were recorded on a FTIR-8400S Infrared spectrophotometer SHIMADZU using KBr pellets. Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a Bruker (ARX-500) spectrophotometer (400 MHz) in DMSO-d$_6$, using tetramethylsilane (TMS) as internal standard, chemical shifts (δ) given in ppm. The mass spectra were recorded on ESITOF MS mass spectrometer and Ultraviolet-visible (UV–vis) absorption spectra were recorded on a UV-1650 PC UV-visible spectrophotometer SHIMADZU. Cyclic voltammograms were studied in Model EA201 Electro Analyser (Chemi Link Systems) and were carried out at room temperature using glassy carbon electrode, Platinum electrode and saturated calomel electrode as the working, counter and reference electrode. All reactions were monitored by thin-layer chromatography and experiments were repeated at least in triplicates. The chemicals used for the synthesis were of analytical reagent grade and was used without further purification. The solvents were of spectroscopic grade.

Synthesis: General procedure for the preparation of diazonium chloride solutions of (1a-1j) amines: The desired aromatic amine, aniline **1a** (1g - 0.0107 mol) was dissolved in a mixture of concentrated hydrochloric acid (10 ml) and distilled water (15 ml). A solution of sodium nitrite (0.92g - 0.0133 mol) in distilled water (3 ml) was prepared and added dropwise to the acidic solution of amine over a period of 10 min at 0°C, the mixture was stirred at 0°C for 50 min.

General procedure for the preparation of diazo derivatives of cardanol through direct diazo coupling: The pH of preferred diazonium chloride solutions of amines was adjusted to 6.5 and 8 by the addition of appropriate amount of sodium bicarbonate (1 M) solution using digital pH meter MK V1 (Systronics). The pre-cooled solution of cardanol (3.21g – 0.0107 mol) in ethanol (15 ml) was injected dropwise to the above pH monitored solution at 0°C. The reaction mixture was stirred at 0°C for 40 min by which time the product was precipitated. The water insoluble layer was extracted with diethyl ether; the organic layer was washed (2-3 times) repeatedly with 50 ml distilled water and solvent was removed under reduced pressure. The resulting oily viscous dyes **2a-2j** (figure 2) was dried at 50°C for 2 hours.



Entry	Amines	R	Dyes
1	**1a**	-H	**2a**
2	**1b**	-CH$_3$	**2b**
3	**1c**	-Br	**2c**
4	**1d**	-NO$_2$	**2d**
5	**1e**	-COOC$_2$H$_5$	**2e**
6	**1f**	-OCH$_3$	**2f**
7	**1g**	-Cl	**2g**
8	**1h**	-NHCOCH$_3$	**2h**
9	**1i**	-COOH	**2i**
10	**1j**	-F	**2j**

Figure-2
Structure of amines used and cardanol dyes synthesized

4-(Phenylazo)-cardanol (2a): Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$, DMSO d$_6$, TMS) δ: 9.1 (OH), 7.77 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 6.98 (br s, 1H), 6.74 (dd, *J* = 2.0 Hz, 1H), 5.80 (m, CH=CH$_2$ of cardanol), 5.30 (m, olefinic proton of cardanol), 5.20 (m, CH=CH$_2$ of cardanol), 3.02 (t, *J* = 7.6 Hz), 2.90 (m, =CHCH$_2$CH= of cardanol), 2.76 (t, *J* = 7.2 Hz), 2.0 (m, =CHCH$_2$), 1.60 (t), 1.20 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr, cm^{-1}): 3346, 3008, 2923, 2852, 1600, 1483, 1468, 1455, 1365, 1225; MS; m/z = 407.6 (M+1) (derivative of cardanol b), m/z = 404.3 (M+1) (derivative of cardanol c), m/z = 403.3 (M+1) (derivative of cardanol d).

4-(4-methyl-phenylazo)-cardanol (2b): Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS) δ: 9.2 (OH), 7.70 (d, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.99 (d, 1H), 6.69 (br d, *J* = 2.4 Hz, 1H), 5.70 (m, CH=CH$_2$ of cardanol), 5.30 (m, olefinic proton of cardanol), 4.90 (t, CH=CH$_2$ of cardanol), 3.0 (t, *J* = 7.2 Hz), 2.90 (m, =CHCH$_2$CH= of cardanol), 2.60 (t, *J* = 6.0 Hz), 2.35 (s, Ar-CH$_3$), 1.8-1.9 (m, =CHCH$_2$), 1.5 (m, CH$_2$ of cardanol), 1.10 (m), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3350, 3009, 2922, 2860, 1591 , 1465, 1401, 1365, 1296, 1226; MS; m/z = 421.6 (M+1) (derivative of cardanol b), m/z = 419.5 (M+1) (derivative of cardanol c), m/z = 417.7 (M+1) (derivative of cardanol d).

4-(4-bromo-phenylazo)-cardanol (2c): Reddish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 7.85 (d, 2H), 7.70 (d,1H), 7.57 (d, *J* = 6.4 Hz, 1H), 7.09 (br t, *J* = 8.4 Hz, 1H), 6.98 (br s, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 2.0 Hz, 1H), 6.55 (*J* =

10.8 Hz, 1H), 5.70 (m, CH=CH$_2$ of cardanol), 5.30 (m, olefinic proton of cardanol), 4.90 (m, CH=CH$_2$ of cardanol), 3.0 (t, *J* = 7.2 Hz), 2.90 (m, =CHCH$_2$CH= of cardanol), 2.43 (t, *J* = 7.6 Hz), 1.90 (m, =CHCH$_2$), 1.60 (m), 1.40 (m, CH$_2$ of cardanol), 0.70 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}) : 3370, 3010, 2938, 2852 , 1580, 1487, 1480, 1463, 1365, 1225, 1154, 540; MS; m/z = 486.6 (M+1) (derivative of cardanol b), m/z = 484.6 (M+1) (derivative of cardanol c), m/z = 482.5 (M+1) (derivative of cardanol d).

4-(4-nitro-phenylazo)-cardanol (2d): Dark yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 9.2 (OH), 8.37 (d, 2H), 7.95 (d, 2H), 7.76 (d, 1H), 6.84 (d, 1H), 6.74 (br d, *J* = 2.4 Hz, 1H), 5.80 (m, CH=CH$_2$ of cardanol), 5.34 (m, olefinic proton of cardanol), 4.91 (m, CH=CH$_2$ of cardanol), 3.03 (t, *J* = 7.6 Hz), 2.73 (m, =CHCH$_2$CH= of cardanol), 2.69 (t, *J* = 6.8 Hz), 1.9 (m, =CHCH$_2$), 1.60 (t), 1.20 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3380, 3013, 2899, 2827, 1600,1529 , 1485, 1480, 1463, 1402 , 1227, 1339; MS; m/z = 452.8 (M+1) (derivative of cardanol b), m/z = 450.6 (M+1) (derivative of cardanol c), m/z = 448.5 (M+1) (derivative of cardanol d).

4-(4-ethoxy crabonyl-phenylazo)-cardanol (2e): Dark orange-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 9.2 (OH), 7.93 (d, 2H), 7.76 (d,1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.2 Hz,1H), 6.77 (br s, *J* = 6.4 Hz,1H), 6.51 (dd, *J* = 7.2 Hz, 1H), 5.77 (m, CH=CH$_2$ of cardanol), 5.33 (m, olefinic proton of cardanol), 5.01 (m, CH=CH$_2$ of cardanol), 3.10 (t), 2.71 (m, =CHCH$_2$CH= of cardanol), 2.63 (t), 2.0 (m, =CHCH$_2$), 1.60 (t), 1.35 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3420, 3005, 2943, 2842, 1700, 1660, 1610, 1477, 1464, 1446, 1405, 1227, 1163; MS; m/z = 479.8 (M+1) (derivative of cardanol b), m/z = 477.7 (M+1) (derivative of cardanol c), m/z = 475.8 (M+1) (derivative of cardanol d).

4-(4-methoxy-phenylazo)-cardanol (2f): Dark brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 9.1 (OH), 7.77 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 1H), 6.71 (d, 2H), 6.66 (br d, *J* = 6.4 Hz, 1H), 5.80 (m, CH=CH$_2$ of cardanol), 5.31 (m, olefinic proton of cardanol), 4.92 (m, CH=CH$_2$ of cardanol), 3.76 (s, Ar-O-CH$_3$), 3.25 (t), 2.90 (m, =CHCH$_2$CH= of cardanol), 2.68 (t, *J* = 5.6 Hz), 1.91 (m, =CHCH$_2$), 1.62 (m), 1.35 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol and Ar-CH$_3$); IR (KBr cm^{-1}): 3400, 3010, 3090, 2923, 2842, 1640, 1484, 1463, 1398, 1366, 1247, 1181; MS; m/z = 437.6 (M+1) (derivative of cardanol b), m/z = 435.7 (M+1) (derivative of cardanol c), m/z = 433.5 (M+1) (derivative of cardanol d).

4-(4-chloro-phenylazo)-cardanol (2g): Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 9.1 (OH), 7.76 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.02 (d, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.75 (br d, *J* = 9.2 Hz, 1H), 6.52 (dd, 1H), 5.80 (m, CH=CH$_2$ of cardanol), 5.35 (m, olefinic proton of cardanol), 5.18 (m, CH=CH$_2$ of cardanol), 3.0 (t, *J* = 7.2 Hz), 2.90 (m, =CHCH$_2$CH= of cardanol), 2.66 (t, *J* = 7.6 Hz), 1.97 (m, =CHCH$_2$), 1.78 (m), 1.49 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3360, 3008, 2908, 2851, 1680, 1493, 1463, 1400, 1365, 1174, 1154, 620; MS; m/z = 442.2 (M+1) (derivative of cardanol b), m/z = 440.1 (M+1) (derivative of cardanol c), m/z = 438.2 (M+1) (derivative of cardanol d).

4-(4- acetamide-phenylazo)-cardanol (2h): Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 10.1 (NH), 9.1 (OH), 7.73 (d, 2H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.0 (t, 1H), 6.72 (br s, *J* = 2.4 Hz, 1H), 6.65 (dd, 2H), 5.76 (m, CH=CH$_2$ of cardanol), 5.31 (m, olefinic proton of cardanol), 4.92 (m, CH=CH$_2$ of cardanol), 3.0 (t, *J* = 7.2 Hz), 2.96 (m, =CHCH$_2$CH= of cardanol), 2.72 (t, Ar-NH-C-O-CH$_3$), 1.67 (m, =CHCH$_2$), 1.78 (t), 1.35 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3420, 3015, 3354, 2912, 2837, 1720, 1601, 1483, 1463, 1404, 1371, 1151; MS; m/z = 464.6 (M+1) (derivative of cardanol b), m/z = 4462.7 (M+1) (derivative of cardanol c), m/z = 460.6 (M+1) (derivative of cardanol d).

4-(4- carboxylic acid-phenylazo)-cardanol (2i): Reddish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 10.1 (COOH), 9.1 (OH), 7.82 (d, *J* = 7.2 Hz, 2H), 7.61 (t, 1H), 7.57 (t, *J* = 8.8 Hz, 2H), 6.74 (br s, *J* = 2.0 Hz, 1H), 6.69 (dd , *J* = 6.4 Hz, 1H), 5.80 (m, CH=CH$_2$ of cardanol), 5.32 (m, olefinic proton of cardanol), 5.07 (m, CH=CH$_2$ of cardanol), 3.0 (t, *J* = 7.2 Hz), 2.97 (m, =CHCH$_2$CH= of cardanol), 2.67 (t, *J* = 6.4 Hz), 2.44 (m, =CHCH$_2$), 1.96 (t, *J* = 3.6 Hz), 1.2 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3350, 3001, 2907, 2847, 1740, 1620, 1486, 1455, 1426, 1366, 1231, 1153; MS; m/z = 451.7 (M+1) (derivative of cardanol b), m/z = 449.6 (M+1) (derivative of cardanol c), m/z = 447.5 (M+1) (derivative of cardanol d).

4-(4-fluoro-phenylazo)-cardanol (2j): Dark yellow viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 9.1 (OH), 7.84 (d, *J* = 8.4 Hz, 2H), 7.70 (d, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.51 (d, 2H), 6.49 (br d, 1H), 5.75 (m, CH=CH$_2$ of cardanol), 5.32 (m, olefinic proton of cardanol), 5.02 (m, CH=CH$_2$ of cardanol), 3.30 (t), 2.73 (m, =CHCH$_2$CH= of cardanol), 2.55 (t), 1.90 (m, =CHCH$_2$), 1.67 (m), 1.41 (m, CH$_2$ of cardanol), 0.80 (m, CH$_3$ of cardanol); IR (KBr cm^{-1}): 3400, 3060, 2923, 2826, 1600, 1499, 1466, 1444, 1365, 1228, 1153, 1090; MS; m/z = 424.6 (M+1) (derivative of cardanol b), m/z = 423.8 (M+1) (derivative of cardanol c), m/z = 421.7 (M+1) (derivative of cardanol d).

Results and Discussion

Synthesis: Many factors in cardanol diazocoupling reactions serve to lower the yield of azo compounds. Given, the nature of cardanol and diazonium salts, these factors are normally obligatory. The method of controlling the pH of the reaction mixture and maintaining the coupling reaction to takes place at slightly acidic media (pH – 6.5) affords appreciable yields (>85%). Oxidation of cardanol becomes gradually quick with increase in alkaline pH. However, a high pH also upsurges the reactivity of cardanol to diazocoupling. It is the balancing of these two physiognomies of cardanol which leads to compromises to the yield of diazo coupling reaction.

The result from the table 1 indicated that the dependency of the yield of diazo compounds on the nature of the diazonium salt is in agreement with the principle that electron withdrawing groups increase the reactivity of diazonium salts. However, these groups also promote the ability of the diazonium salts to accept an electron in hemolytic dediazotization reactions[12]. To the extent that the reactivity of the diazonium salts is enhanced by electron withdrawing moieties, we can expect the good yield of diazo compounds.

Table-1
Corresponding percentage yield of dyes at pH 6.5 and 8

Dyes	**pH**	
	6.5	**8**
2a	86	68
2b	81	64
2c	89	67
2d	92	69
2e	82	57
2f	82	51
2g	85	59
2h	80	71
2i	88	68
2j	83	63

UV-vis absorption studies: The UV-visible spectra of cardanol azo dyes were recorded in the range of 290-600 nm by using different solvents with variable concentrations (0.166µM – 0.196µM) such as dry dimethyl formamide, ethanol and dry hexane. Spectral details for cardanol azo dyes (**2a-2j**) derived from various aniline derivatives (**1a-1j**) has been summarized in table 2.

The position of the bands is strongly influenced by the structure of compounds, for example, by the type of substitution pattern in the donor and acceptor moieties. Communication between the electron donating and accepting terminal groups can be evaluated by comparing the λ_{max} values. In general, stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states and expecting longer wavelength of absorption. From the table 2 it is revealed that dyes **2d** and **2i** do not contain an electron donating functional group in *p*- position, so that λ_{max} is hypsochromic in corresponding dyes **2b**, **2c**, **2e**, **2f**, and **2g** containing $-CH_3$, -Br, $-COOC_2H_5$, $-OCH_3$, and -Cl groups in *p*-position.

Cyclic voltammetric studies: Irreversible electrochemical character of dyes 2a-2j at glassy carbon electrode: Electrochemical behavior of **2a-2j** was investigated by using cyclic voltammetry in sulfuric acid media. These are electroactive species with an azo group (-N=N-) in their molecular structure. This azo group is easily reduced on glassy carbon electrode by cyclic voltammetry. Cyclic voltammogram of 2mM solution of **2a** (analyte) was recorded in sulfuric acid media of 200mM (figure 3) at 100mV/s scan rate. The irreversibility was confirmed by absence of anodic peak in voltammogram between the potential of + 200mV to – 500mV. The voltammogram of **2a** showed reductive peak at -252mV potential. The reduction mechanism of **2a** was illustrated as shown in figure 4. Similarly, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i,** and **2j** were reduced at a potential of -259, -351, -146, -274, -340, -343, -407, -337, and -379mV at 100mV/s scan rate respectively because of the presence of diverse functional groups present in these compounds.

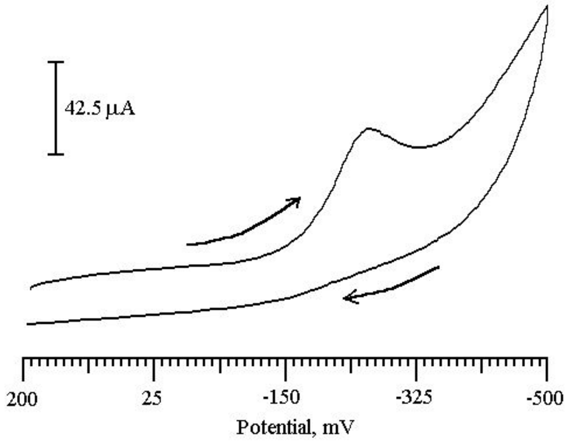


Figure-3
Cyclic Voltammogram of 2mM 2a in 200mM at 100mV/s

Effect of scan rate: Effect of scan rate was studied by placing 2mM of stock solution and 200mM of sulfuric acid in an electrochemical cell. Cyclic voltammetric behavior of **2a** was studied by varying the scan rate from 20mV/s to 120mV/s. The reductive peak current increased with the increase of the scan rate. The plot of current vs. square root of scan rate showed straight line with correlation coefficient 0.9081. This indicates that the electrode reaction of **2a** was controlled by diffusion process[13]. Peak potential was found to shift in the cathodic direction with increase in scan rate indicating the irreversible nature of the electrode reaction[12-14]. Similarly, effect of scan rate was also carried out for compounds **2b-2j**. The correlation co-efficient of dyes from **2a-2j** are set out in table 3. figure 5 shows the plot of cathodic peak potential vs. dyes and the electron withdrawing groups have lower reduction potential when compare to electron donating groups. This technique also gives information about the effect of substituents present in the title azo compounds.

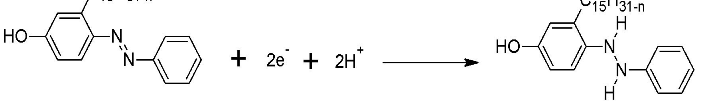


Figure-4
Reduction mechanism of 2a

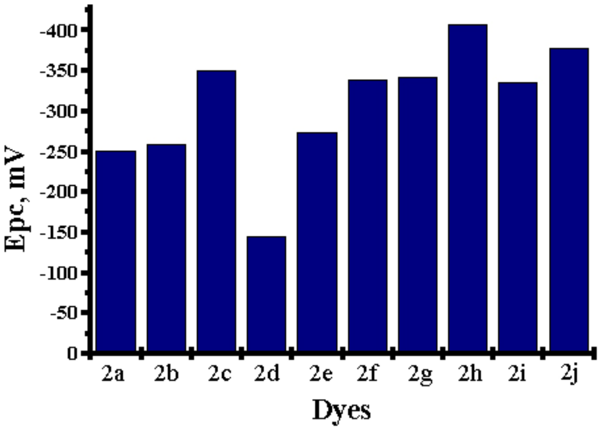


Figure-5
Shows the graphical representation of potential vs. cardanol dyes

Effect of concentration of analyte 2a: The voltammogram of **2a** showed an excellent reductive peak. The concentration effect of this compound was studied by varying the concentration of stock solution and keeping the sulfuric acid concentration constant through out the measurement. Voltammograms for different concentration of **2a** was recorded as shown in figure 6a. The reductive peak currents were going on enhancing from 0.5mM to 3.0mM of stock solution with shifting in peak potential from -251mV to -351mV. This kind of peak shift with concentration of analyte indicated that the product of analyte molecule is adsorbed over the electrode surface[14]. A representative plot of current as a function of concentration of **2a** is provided in Figure 6b showing linear increase in current.

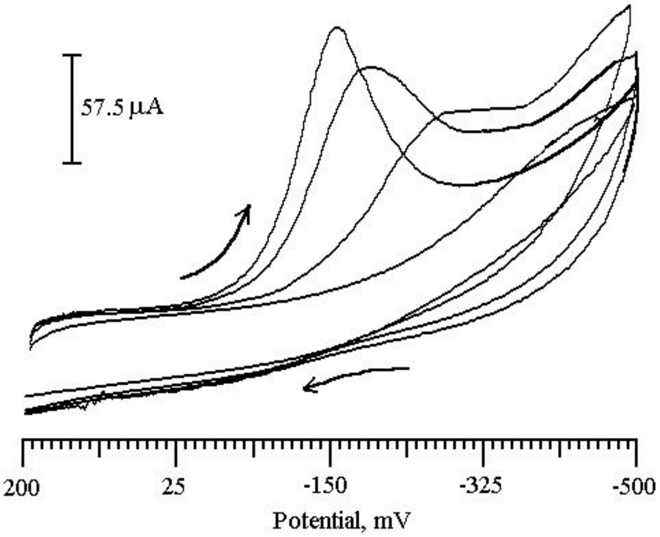


Figure-6a
Cyclic voltammogram of different concentration of 2a

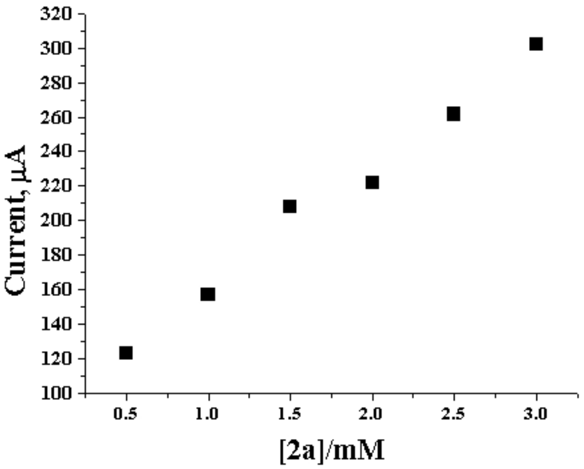


Figure-6b
Graph of current vs. concentration of 2a

Effect of concentration of sulfuric acid: Electrocatalytic reduction of compound **2a** was carried out in different concentration of sulfuric acid. Voltammograms for various concentration of sulfuric acid was recorded (figure 7a). The cathodic peak current was going on enhancing from 50mM to 250mM concentration of sulfuric acid with small shift in peak potential. The cathodic peak potential was shifted towards positive direction from -384 mV to -272 mV because acidic media favors the reduction[15] and increase in the concentration of acid will easy the reduction by taking less potential. The graph of current vs. concentration of sulfuric acid was plotted (figure 7b) showing linear increase in current with the increase of concentration of sulfuric acid.

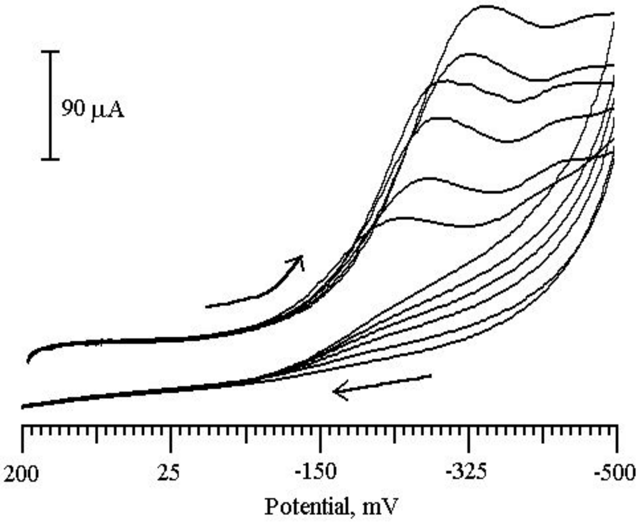


Figure-7a
Cyclic voltammogram for the different concentration of sulfuric acid for 2a

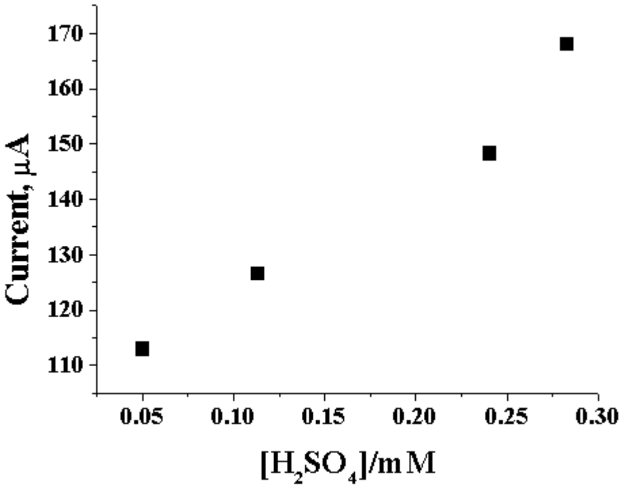


Figure-7b
Graph of current vs. concentration of sulfuric acid

Conclusion

In summary, ten azo dyes containing cardanol as coupling component were synthesized using classical diazotization coupling reaction with preferable modification in the pH of the coupling reaction at slightly acidic condition (pH – 6.5) and all the dyes were individually characterized by spectroscopic techniques (FT-IR, ESITOF MS, UV and ^{1}H NMR). The result indicated from cyclic voltammetric studies is that, the peak potential was found to shift in the cathodic direction with increase in scan rate indicating the irreversible nature of the electrode reaction. The dyes showed irreversible one step two electron diffusion controlled reduction processes.

Acknowledgment

The author (Husnasarvari Maqbool) is grateful to UGC for providing Moulana Azad Research Fellowship. The author is grateful to Indian Institute of Science Bangalore and STIC for spectral analysis.

Table-2
UV – visible spectral details for cardanol azo dyes 2a-2j

	Hexane		DMF		Ethanol	
Dyes	**λmax(nm)**	**Absorbance**	**λmax(nm)**	**Absorbance**	**λmax(nm)**	**Absorbance**
2a	347.0	0.33	362.9	0.35	359.1	0.68
2b	349.6	0.27	363.3	0.52	360.0	0.78
2c	356.5	0.30	371.2	0.13	366.9	0.56
2d	373.8	0.20	392.0	0.50	392.0	0.84
2e	361.0	0.29	392.5	0.49	376.7	0.67
2f	356.5	0.33	369.5	0.55	365.5	0.94
2g	355.6	0.20	371.2	0.18	366.0	0.40
2h	361.7	0.40	375.6	0.46	371.2	0.76
2i	367.7	0.18	385.1	0.13	379.9	0.23
2j	347.8	0.33	363.8	0.36	358.2	0.70

Table-3
Correlation co-efficient of dyes 2a-2j

Dyes	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**
Correlation co-efficient	0.9081	0.9484	0.9770	0.8955	0.9367	0.9508	0.9880	0.9934	0.8800	0.9935

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