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Studies on physicochemical properties of azo cardanol sulfonates and their salts

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ABSTRACT

The densities, relative viscosities and surface tensions of some selected cardanol based azo dyes were determined. The sodium, ammonium and diethanolamine salts of the respective dyes were successfully synthesized after selective sulfonation. All these compounds were studied and characterized using Fourier Transform Infrared Spectroscopy (FTIR), Liquid chromatography–mass spectrometry (LCMS), UV-Visible Spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopic techniques. The densities and surface tensions of all the cardanol sulfonate salts were in the range 0.947 g/mL and 32.15–36.79 dynes/cm respectively. The relative viscosities were in the range 1.272 – 1.484.

INTRODUCTION

Cashew Nut Shell Liquid (CNSL) is one of the low cost, bio based, naturally occurring resources of non-isoprenoid phenolic lipids consisting cardanol as a chief constituent [1]. CNSL is essentially a mixture of four phenolic constituents specifically anacardic acid, cardol, cardanol and 2-methylcardol, the commercial vacuum distillation of cashew nut shell liquid finally affords cardanol in major yeild. 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 [2]. The structure resemblances of these phenolic constituents with various petrochemicals with special surface active properties were of continuum interest [3]. The cardanol sulfonates and their salts find delightful applications conveniently in pulp and paper industries as these compounds shows preferable detergent, penetrating, wetting and dispersing properties [4]. The polyketide unsaturated side chain with azo dye linkages in addition to the sulfonic acid moieties makes these structures still more interesting as surface active agents [5] and petroleum markers [6] for coloration and textile dyeing.

The eco-friendly and biodegradable nature of these cardanol and its derivatives have innumerable applications in polymer based industries such as, paints, varnishes, wood preservatives, surfactants, epoxy resins and laminating resins. Because of their unique antioxidant properties, derivatives of cardanol and phosphorated cardanol catch the attention of the material engineers for gasoline stabilization [7]. Variations of mechanical and electrical properties of styrene butadiene styrene/polyaniline copolymer blends are easily controlled by the cardanol as the plasticizers [8]. Structure and properties of various liquid crystalline materials, bio-based amphiphiles based on cardanol were also reported in recent years [9]. The new reliable research and development also engrossed by the insertion of these cardanol into supra molecules for instance porphyrins [10-13], phthalocyanine [14] and fullerene [15].

Today, a variety of emerging scientific and methodological developments have been reported that aim to improve practical applications of petroleum marker dyes [16].These developments can facilitate how synthetic targets or materials are prepared and used. The cost effectiveness of these hi-tech dyes can be reduced by developing the bio-based low cost material incorporation such as cardanol.

In this contextual, the diesel fluorescent marker dyes were synthesized and applied potentially as compared in contrast to the emerging hi-tech dyes [17]. Azo dyes derivatives with synthetic cardanol formaldehyde resins were greatly expanded and broadly impacted in the polymer science and technology field [18].

In this article, we report the synthesis of cardanol based azo dyes using aniline and substituted anilines. These dyes were carefully sulfonated by using oleum (20% SO_3) with conditional variations of suitable parameters such as temperature, reaction time, agitation and retention time of sulfonation. The salts (sodium, ammonium and diethanolamine) of these azo derivatives were prepared with controlling similar aforementioned conditions and physicochemical properties were studied in detail.

MATERIALS AND METHODS

Materials

Cashew nut shell liquid (CNSL) and Cardanol were received from Cashitrons Resins Pvt.Ltd., Ankola, Oleum (20% SO_3) and diethanolamine were procured from Sigma Aldrich and used as received. All the other chemicals were of reagent grade and used without further purification.

Synthesis

General procedure for the preparation of diazo derivatives of cardanol

The synthesis of 4-(Phenylazo)-cardanol is discussed. The typical procedure is as follows. Aniline (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 drop wise 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.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 drop wise 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 **1-4** were dried in vacuum oven at 50 °C for 2 hours.

4-(Phenylazo)-cardanol (1)

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), m/z = 404.3 (M+1), m/z = 403.3 (M+1).

4-(4-nitro-phenylazo)-cardanol (2)

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), m/z = 450.6 (M+1), m/z = 448.5 (M+1).

4-(4-methyl-phenylazo)-cardanol (3)

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), m/z = 419.5 (M+1), m/z = 417.7 (M+1).

4-(4-fluoro-phenylazo)-cardanol (4)

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), m/z = 423.8 (M+1), m/z = 421.7 (M+1).

General procedure for the sulfonation of diazo derivatives of cardanol

The desired diazo derivatives of cardanol (1g) were dissolved in methanol (6 mL) in a 100 mL round bottom flask fitted with a nitrogen inlet and outlet and a mechanical stirrer. The methanolic dye solution was cooled to -20 $^{\circ}$C. To this cold stirring solution, the oleum (0.2 mL) in a glass syringe was added very slowly over a period of 10 min. The temperature of reaction mixture was maintained at -20 $^{\circ}$C for about 30 min with proper continues stirring (Additional 2 mL of dry methanol was added for worthy stirring of the reaction mixture). The contents of the flask were kept constant for further 10 min, after the retention time the reaction mixture was immediately washed with 20 mL cold water (< 10 $^{\circ}$C) to avoid polymerization, unreacted oleum was removed by effective washing in cold water. Thick viscous moisture sensitive sulfonated cardanol dyes were instantly filtered and stored under nitrogen.

Sulphonated 4-(Phenylazo)-cardanol (5)

Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_{Z,}$ DMSO d$_6$, TMS) δ: 8.3 (SO$_3$H), 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, 1154.37 (S=O, asym.), 1042.24(S=O, sym.); MS; m/z = 481.6 (M-1), m/z = 483.6 (M-1), m/z = 485.6 (M-1).

Sulphonated4-(4-nitro-phenylazo)-cardanol (6)

Dark yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 8.4 (SO$_3$H), 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, 1104.86 (S=O, asym.), 1043.99(S=O, sym.); MS; m/z = 526.6 (M-1), m/z = 528.6 (M-1), m/z = 530.6 (M-1).

Sulphonated4-(4-methyl-phenylazo)-cardanol (7)

Yellowish-brown viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS) δ: 8.4 (SO$_3$H), 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, 1158.77 (S=O, asym.), 1045.32 (S=O, sym.); MS; m/z = 495.6 (M-1), m/z = 497.6 (M-1), m/z = 499.6 (M-1).

Sulphonated4-(4-fluoro-phenylazo)-cardanol (8)

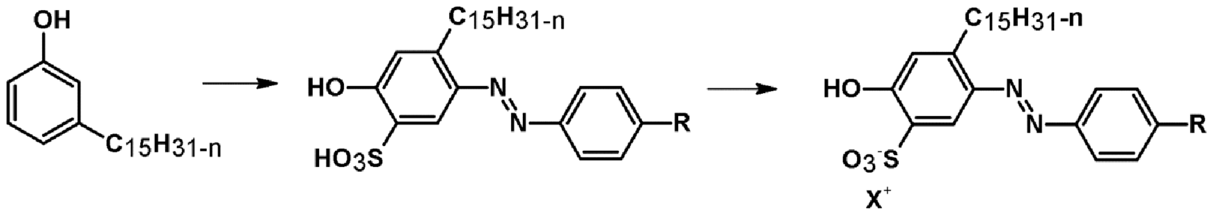
Dark yellow viscous liquid; ^{1}H NMR (400 MH$_Z$; DMSO d$_6$, TMS): 8.0 (SO$_3$H), 9.1 (OH), 7.84 (d, *J* = 8.4 Hz, 2H), 7.70 (d, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.51 (d, 2H), 6.49 (br d, 1H),5.75 (m, CH=CH$_2$ of cardanol), 5.32 (m, olefinic proton of cardanol), 5.02 (m, CH=CH$_2$ of cardanol), 3.30 (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, 1152.71 (S=O, asym.), 1043.04(S=O, sym.); MS; m/z = 499.6 (M-1), m/z = 501.6 (M-1), m/z = 503.6 (M-1).

General procedure for the preparation of salts

The salts of diazo cardanol sulfonates were prepared from sulfonation of diazo derivatives of cardanol within the temperature range of 0–10 °C by using appropriate basic solutions of 10% sodium hydroxide (for sodium salts), 1:1 ammonia solution (for ammonium salts) and 1:1 diethanolamine solution (for diethanolamine salts). The typical procedure for the sodium salt of diazo cardanol sulfonate was discussed below.

In a 100 mL Erlenmeyer flask, 10% of sodium hydroxide (10 mL) was added to the sulfonated 4-(Phenylazo)-cardanol and the reaction mixture was continuously stirred for 15 h on a shaker below 10 °C. The pH of the resulting solution was kept above 8 by adding additional 2 mL of sodium hydroxide after 20 h. The mixture was kept agitated with keeping the pH of solution maintained at 8. The reaction mixture was sonicated for 30 min and filtered. Thick pasty salt was moisture sensitive and stored under nitrogen.

Correspondingly, ammonium and diethanolamine salts were prepared by using appropriate 1:1 ammonia solution and 1:1 diethanolamine solution to afford respective salts. For compound **5**, three salts are prepared, namely sodium, ammonium and diethanolamine, designated as **5a**, **5b** and **5c** respectively. Similar designations are followed for compound **6**, **7** and **8**. Scheme is shown in Figure 1.



where, n = 0, 2, 4 and 6.

R = H, NO_2, CH_3 and F.

X = Na, NH_3 and $(CH_2CH_2OH)NH_2$.

Figure 1.Synthetic route to prepare azo dye cardanol sulfonate salts

RESULTS AND DISCUSSION

As we know the fresh extracted CNSL is yellowish thick red/brown and is get darkened during storage because of air oxidation. Cardanol is sensitive to air and the sulfonation of this is a challenging synthetic strategy because it easily polymerises in the conditions prescribed in the literature [2]. Diazo coupling was done in slightly acidic conditions (at pH 6.5) to afford appreciable yield (>85%), this is due to oxidation of cardanol (more rapid in alkaline pH). Oleum is used for the sulfonation of dye compounds and maintained the temperature below -20 °C to avoid side polymeric reactions. The dye cardanol sulfonates and their respective salts are highly air and moisture sensitive so the reactions are done under inert atmosphere and final compounds were stored under nitrogen.

The UV-visible spectra of cardanol azo dyes and dye sulfonate salts were recorded in the range of 200-800nm in dimethyl formamide (DMF) solvent with concentration (0.001M). $–CH_3$ and –F substituents of the ammonium salts shows maximum absorbance compared to the –H and $–NO_2$ substituents and UV-Vis plots were presented in the Figure 2.

Surface tensions for all the salts were determined at room temperature with a Japan Kaimenkaguka CBVP-A3 surface tensiometer. The results were tabulated in Table 1.

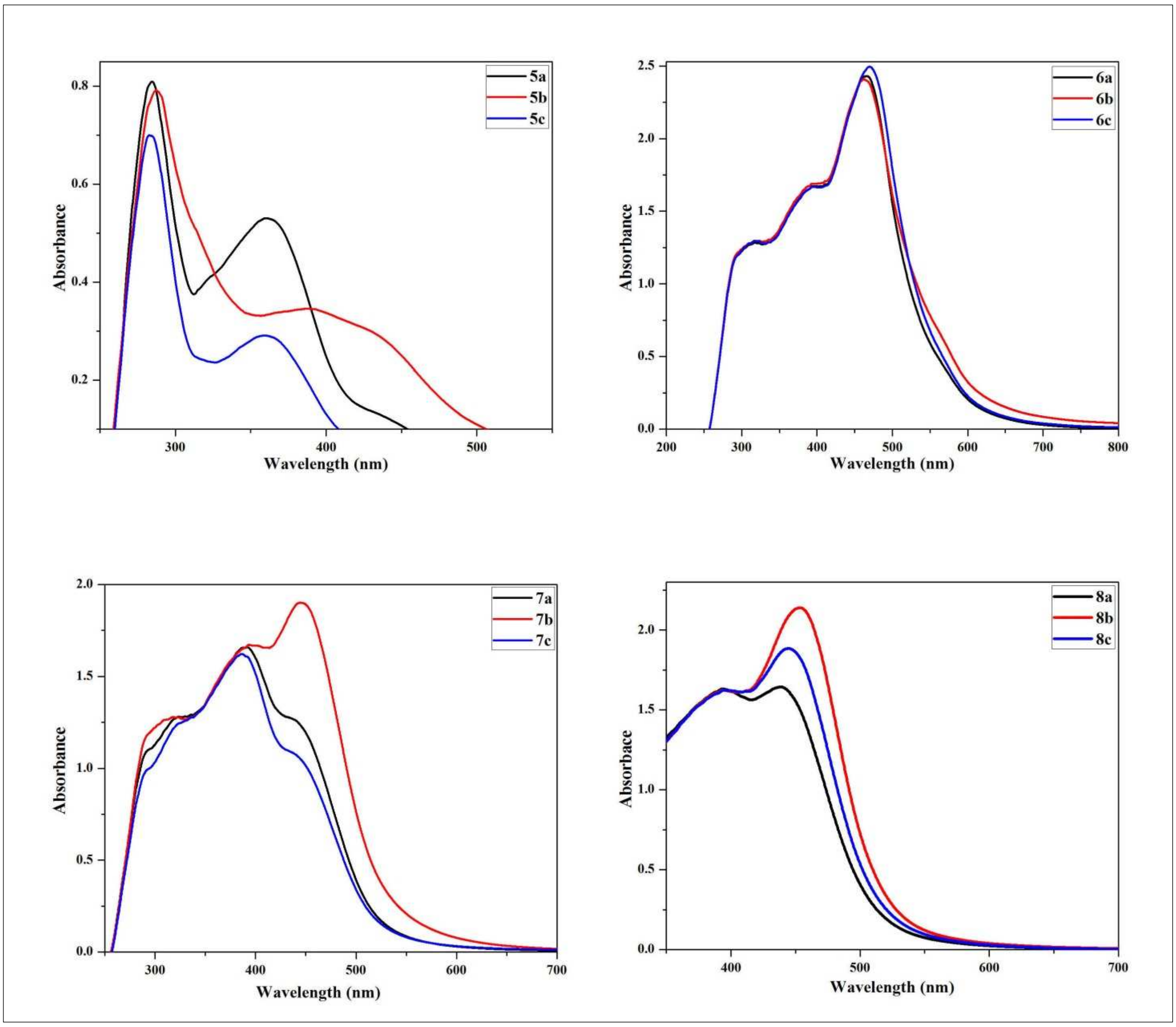


Figure 2. UV-Vis Plots of azo dye cardanol sulfonate salts

Table 1: Relative viscosity and surface tensions of the dye sulfonate salts

Compound	Relative Viscosity	Surface Tension (dynes/cm)
5a	1.363	36.39
5b	1.454	32.15
5c	1.373	36.79
6a	1.464	34.14
6b	1.454	35.23
6c	1.474	36.40
7a	1.464	34.86
7b	1.272	34.14
7c	1.464	35.33
8a	1.454	35.23
8b	1.484	36.40
8c	1.292	35.99

CONCLUSION

In conclusion, a convenient synthetic route was explored to prepare dye cardanol sulfonates. The sulfonation was achieved in cold condition (-20 °C) to avoid side polymeric reactions. All the dyes and sulfonated dyes were characterized by FTIR, LCMS and ^{1}H NMR spectroscopy. The relative viscosity, surface tensions and UV-Vis spectroscopy of dye cardanol sulfonated salts were determined. These functional dyes are useful in the study of some hi-tech applications.

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