

**Electrochemical Investigation of Lignin Resin Doped with
Different Ratios Rhodamine B**

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Abstract

The electrochemical behavior was investigated of Lignin Resin by using the cyclic voltammetry technique. Such investigation mainly focuses on the expected properties of the doped resin with different doping ratios of Rhodamine B (0.01, 0.5, 0.1, 0.15, 0.2) %wt. This is indicated by the electron transfer between the dopant and resin, which clearly shows the appearance of oxidation – reduction peaks accompanied log increase in electrical current I_p as applied potential changes. The heights of I_p oscillate due to the change in scan rate v . The results of linear of relationships between I_p with $v^{1/2}$ indicated that the electron transfer was a process of one electron transfer.

Keywords: Cyclic voltammetry, Lignin resin, Rhodamine B, supporting electrolyte.

Introduction

Today linear potential scan methods are very useful tools for initial studies of new systems and proved to be reliable techniques to obtain information about fairly complicated electrode reactions. Cyclic voltammetric methods, in particular, have often been used in basic studies of electrochemical systems and in the field of analytical research. Cyclic Voltammetry is obtained by measuring the current between the working and the counter electrode as a function of the potential (normalized to the potential of the reference electrode). To do this, the experimenter uses a three-electron setup and varies the potential of an electrode (the “working” electrode), which is immersed in an unstirred solution, and measures the resulting current [1,2].

A triangular potential sweeps the potential of the working electrode between the starting potential to the switching potential and back again. The scan rate ν (in mV/s) is an important parameter. The current flows in or out of the working electrode to or from a counter electrode. The potential of the working electrode is controlled versus a reference electrode. The reference electrode passes no current [3].

The peak current in a cyclic voltammogram containing only one species is described by Sevcik- Randles [4]:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C^* \quad (1)$$

at 25 °C where I_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, ν is the scan rate and C^* is the bulk concentration of the species. If the diffusion constants for the oxidized and reduced species are similar, the value of E_o' (formal potential) can be estimated from the average of E_{pa} and E_{pc} , where E_{pa} is the potential of the anodic peak current and E_{pc} is the potential of the cathodic current [5].

Experiment

Materials

The materials used in this study were lignosulfonate, hydrochloric acid, formaldehyde, sodium hydroxide, sodium bicarbonate, phosphoric acid, ethanol amine, dimethyl formamide, propanol and Rhodamine B.

Modification method of lignosulfonate

A mixture of lignosulfonate (5gm) and %57 hydrochloric acid then the reaction mixture was heated under reflux for (3hr).after that the reaction mixture is allowed to cooled, the solid precipitate obtained was filtered, washed for many times with Deionized water then dried in the oven at 60°C [6].

Synthesis of lignosulfonate formaldehyde Resin

Modify lignosulfonate (10gm) was added to (15ml) of %10 sodium hydroxide, then the mixture was heated at 80°C for 75 min. After completion of the reaction, the mixture was cooled then solution of formaldehyde (60ml) and sodium bicarbonate (1.6gm) was added, the reaction mixture was heated with stirring at 65°C for 3hr, then the reaction mixture was cooled, neutralized by %10 of phosphoric acid H₃PO₄ to PH = 7 excess solvent was distilled off, the result mixture was dried by heating under vacuum pressure for 24 hr at 40°C [7].

Synthesis of amino resin

Added phosphoric acid (1ml) to ethanol amine (0.1 mole, 6.1 gm), the reaction mixture was heated to 50°C then solution of lignosulfonate formaldehyde Resin (10gm) in little amount of ethanol amine was added drop wise over a period of 30 min at 50°C. After that temperature of reaction increase stepwise to 135°C, the reaction was still at this temperature for 5 hr. Then the excess of ethanol was distilled off. The mixture was cooled and neutralized by saturated solution of sodium bicarbonate, the product was formed dissolved in propanol, filtered off to remove precipitate salt then excess solvent was distilled off under vacuum pressure at 90°C. Purification to obtain pure resin, dried under vacuum pressure at 50°C for 24 hr [8].

Doping of Lignin

Doping lignin resin with dye Rhodamine B is prepared by adding the weighed dye to the appropriate weight of polymer (1g) then the mixture was dissolved in dimethyl formamide DMF after the prepared directly to give a polymer / dye system containing (0.01, 0.05, 0.1, 0.15 and 0.2) g wt% of doping reagent Rhodamine B [9]. The mixture was stirred well for 20 minutes to guarantee that the homogenous distribution of dye in the polymer matrix.

Electrochemical measurements

Cyclic-Voltammetry (CV) was carried out in a thermostated one compartment three-electrode cell. The working electrode was a platinum wire of nominal area 0.0785 cm². This was controlled by silver-silver chloride as a reference electrode through which no current flows. The

auxiliary (secondary) electrode was a platinum wire. Cyclic voltammetry was performed with a DY 2300 Series Potentiostat /Bipotentiostat, potentiostat-galvanostat fully computerized in the processed data analysis.

In cyclic voltammetry (CV), the voltage is linearly varied from initial to final potential values as required and then directly swept back at the same sweep rate to the initial one. The current response is plotted as a function of voltage rather than time. The species were reduced and oxidized in the manner of reversible reactions. During all measurements Bu_4NBF_4 was used as a supporting electrolyte.

In cyclic voltammetry, the negative initial potential value was set mostly equal to the final positive one. The scan rate (v) was varied from 0.1 to 1 Vs^{-1} , while the voltage was scanned between -2 to 2.5 V. The molar concentration of supporting electrolyte Bu_4NBF_4 was 0.1 M. The solutions of pure lignin resin as well as the doped solutions with different weight ratios of Rhodamine B (0.01, 0.05, 0.1, 0.15, 0.2) wt% were all subjected to cyclic voltammogram, in order to achieve a comparison with the measured precursor cyclic voltammograms of pure solutions. All measurements were performed at room temperature.

Results and Discussion

The electrochemical behavior of lignin resin and its doping ratios were established by cyclic voltammetry (CV) for oxidation and reduction at a platinum electrode in DMF at scan rates 0.1 to 2 Vs^{-1} at a potential range of 2 to -2.5 V. At scan rate 0.1 Vs^{-1} two reduction peaks were obtained for lignin resin the first reduction peak at $E_{p_{\text{red}2}} = -0.9$ V corresponding to the cathodic peak current $I_{p_{\text{red}1}} = 2 \times 10^{-5}$ A. The second peak is $E_{p_{\text{red}2}} = -0.33$ V corresponding to the cathodic peak current $I_{p_{\text{red}2}} = 1 \times 10^{-5}$ A, as shown in Figure (1). In this Figure the reduction peak is shifted to higher cathodic potential.

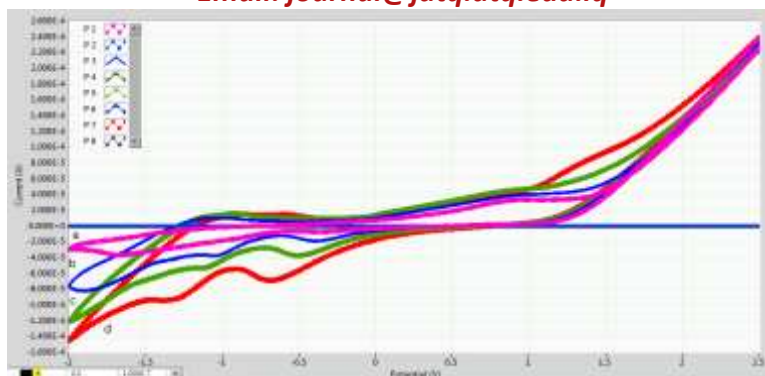


Figure (1): Cyclic voltammogram for lignin resin at scan rates (a) 0.1Vs^{-1} (b) 0.2Vs^{-1} (c) 0.5Vs^{-1} (d) 1Vs^{-1}

According to Sevcik-Randles Equation (1) which gives the relationship between the peak current I_p and the square root of the scan rate $v^{1/2}$, the following graphic relations are established

I_p & $v^{1/2}$

F_p & v

Where $F_p = I_p / v^{1/2}$ and is known as current function. So, both F_p^{red} (reduction) and F_p^{ox} (oxidation) can be computed.

Table (1) shows the values of $I_{p_{\text{rd}}}$ and F_p^{rd} of lignin resin, from which a linear relationship between $I_{p_{\text{rd}}}$ with $v^{1/2}$ was obtained as shown in Figure (2) indicating one electron transfer process, Figure (3) shows the plot of F_p versus v from which it is clear that the F_p is essentially invariant with v provided that $v > 0.1\text{Vs}^{-1}$ a condition which isolates the primary electron transfer from the subsequent chemical step. The independence of F_p is a diagnostic signal of diffusion-controlled electron transfer at specified potentials beyond the peak potential [10,11].

Table (1): Cyclic Voltammogram data of lignin resin at different scan rates.

v $\text{V}\cdot\text{sec}^{-1}$	\sqrt{v} $(\text{Vs}^{-1})^{1/2}$	$I_{p_{\text{red}1}} \text{ A}$ (10^{-4})	$F_p^{\text{red}1}$ $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-4})	$I_{p_{\text{red}2}} \text{ A}$ (10^{-4})	$F_p^{\text{red}2}$ $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-4})
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0.1	0.316	0.2	0.632	1	3.164
0.2	0.447	0.45	1.006	2	4.474
0.5	0.707	0.6	0.848	4	5.657
1.00	1.000	1	1	6.8	6.8

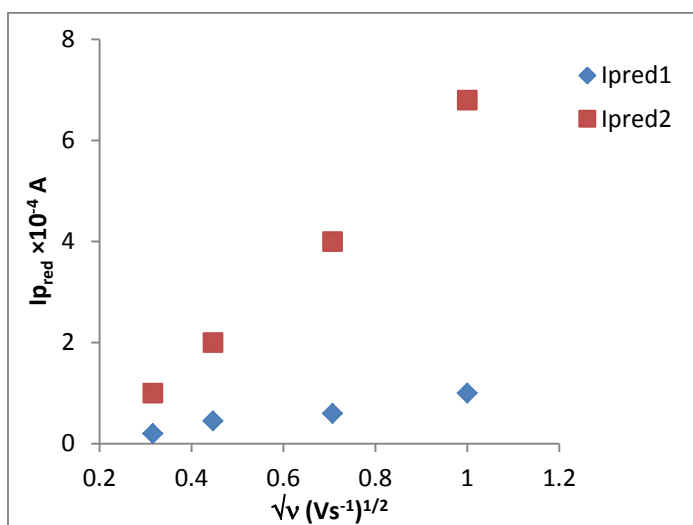


Figure (2): I_{pred1} and I_{pred2} peaks of reduction versus $v^{1/2}$ for lignin resin

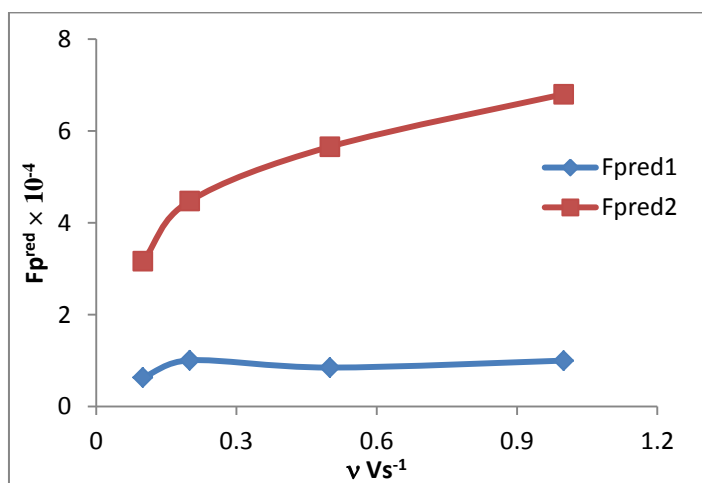


Figure (3): Current function Fp^{red1} and Fp^{red2} versus scan rate for lignin resin

When doping lignin resin with different ratios of dye, notice that the two reduction peaks disappeared while two oxidation peaks appeared with shifted to more positive values as v increases and increase in current value for (0.01, 0.05, 0.1)% doping ratios except 0.15 and 0.2 % ratios it's found decrease in current in this ratios.

Figures (4-6) show the cyclic voltammetry of doping lignin resin with (0.01, 0.05, 0.1)% doping ratios respectively at potential range of 2 to -2.5 V . This figures exhibit two oxidation peaks appeared for this ratios. At $E_{p_{ox}}=0.3V$ corresponding to anodic peak current $I_{p_{ox1}}=7 \times 10^{-5}$ A, and $E_{p_{ox}}=1.6$ V with $I_{p_{ox2}} = 3.3 \times 10^{-4}$ A for 0.01% doping, while at $E_{p_{ox}}=0.4V$ corresponding to anodic peak current $I_{p_{ox1}}=8 \times 10^{-5}$ A, and $E_{p_{ox}}=1.7$ V with $I_{p_{ox2}} = 3.8 \times 10^{-4}$ A for 0.05% doping, and at $E_{p_{ox}}=0.45V$ corresponding to anodic peak current $I_{p_{ox1}}=8 \times 10^{-5}$ A, and $E_{p_{ox}}=1.8V$ with $I_{p_{ox2}} = 4 \times 10^{-4}$ A for 0.01% doping. The overall results of cyclic voltammogram data of 0.01, 0.05 and 0.1 % are given in Tables (2), (3) and (4) respectively.

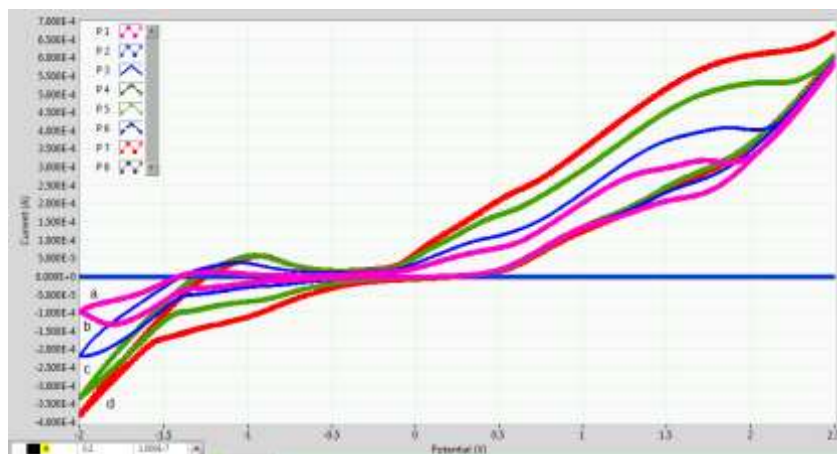


Figure (4): Cyclic voltammogram for 0.01% doping of lignin resin at scan rates (a) $0.1Vs^{-1}$ (b) $0.2 Vs^{-1}$ (c) $0.5 Vs^{-1}$ (d) $1 Vs^{-1}$

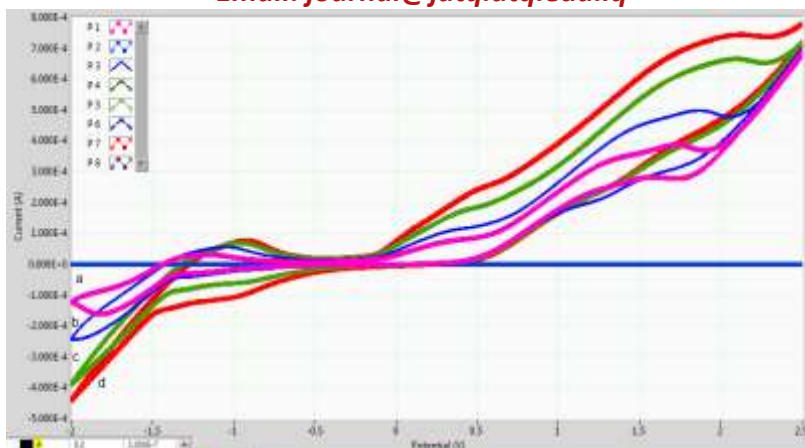


Figure (5): Cyclic voltammogram for 0.05% doping of lignin resin at scan rates (a) 0.1Vs^{-1} (b) 0.2Vs^{-1} (c) 0.5Vs^{-1} (d) 1Vs^{-1}

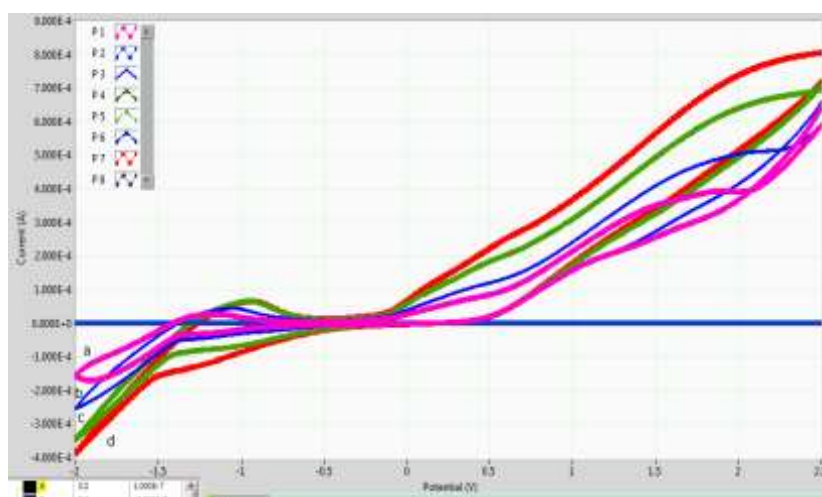


Figure (6): Cyclic voltammogram for 0.1% doping of lignin resin at scan rates (a) 0.1Vs^{-1} (b) 0.2Vs^{-1} (c) 0.5Vs^{-1} (d) 1Vs^{-1}

Table (2): Cyclic Voltammogram data of 0.01% doping of lignin resin at different scan rates

v $\text{V}\cdot\text{sec}^{-1}$	\sqrt{v} $(\text{Vs}^{-1})^{1/2}$	$I_{p_{ox1}}$ A (10^{-4})	Fp^{ox1} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-4})	$I_{p_{ox2}}$ A (10^{-4})	Fp^{ox2} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-4})
0.1	0.316	0.8	2.531	3.3	10.443

0.2	0.447	1	2.237	4	8.948
0.5	0.707	1.4	1.980	5.4	7.637
1.00	1.000	2	2	6.3	6.3

Table (3): Cyclic Voltammogram data of 0.05% doping of lignin resin at different scan rates

v V.sec ⁻¹	\sqrt{v} (V.s ⁻¹) ^{1/2}	$I_{p_{ox1}}$ A (10 ⁻⁴)	Fp^{ox1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁴)	$I_{p_{ox2}}$ A (10 ⁻⁴)	Fp^{ox2} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁴)
0.1	0.316	0.87	2.753	3.8	12.025
0.2	0.447	1	2.237	5	11.185
0.5	0.707	1.5	2.121	6.5	9.193
1.00	1.000	2.2	2.2	7.5	7.5

Table (4): Cyclic Voltammogram data of 0.1% doping of lignin resin at different scan rates

v V.sec ⁻¹	\sqrt{v} (V.s ⁻¹) ^{1/2}	$I_{p_{ox1}}$ A (10 ⁻⁵)	Fp^{ox1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	$I_{p_{ox2}}$ A (10 ⁻⁵)	Fp^{ox2} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)
0.1	0.316	1.1	3.481	4	12.658
0.2	0.447	1.2	2.684	5	11.185
0.5	0.707	1.8	2.545	7	9.900
1.00	1.000	2.5	2.5	8	8

Figures (7-9) show a linear relationship between $I_{p_{ox}}$ with $v^{1/2}$ for the ratios (0.01, 0.05, 0.1)%, indicating that the electron transfer is a process of one electron transfer at every oxidation process and verifying at the same time the linear relation between the intensity of the peaks and $v^{1/2}$ [12].

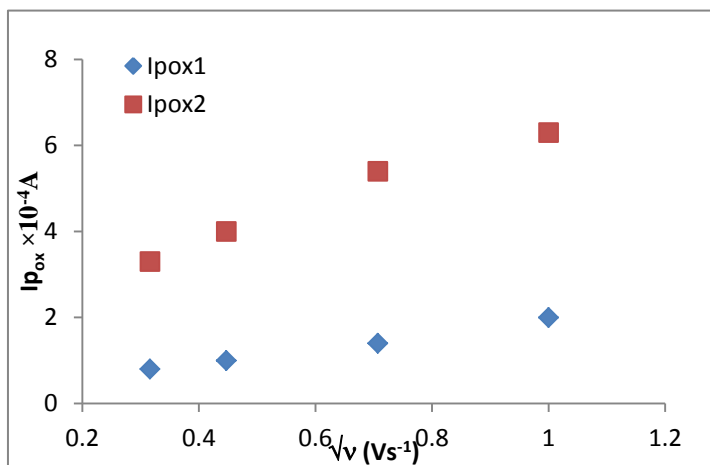


Figure (7): $I_{p_{ox1}}$ and $I_{p_{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.01% doping of lignin resin

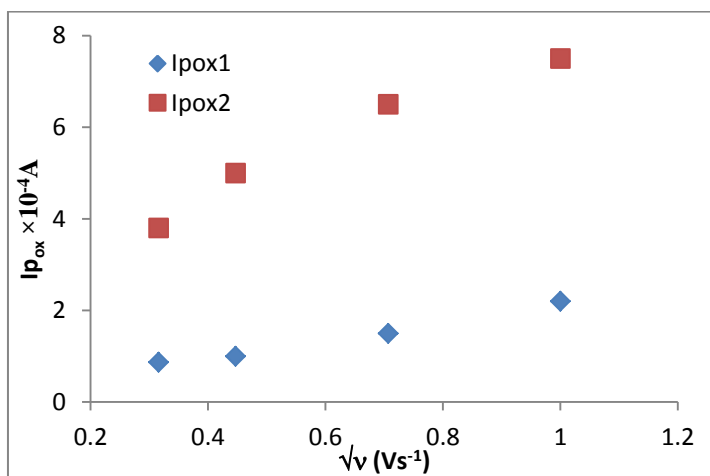


Figure (8): $I_{p_{ox1}}$ and $I_{p_{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.05% doping of lignin resin

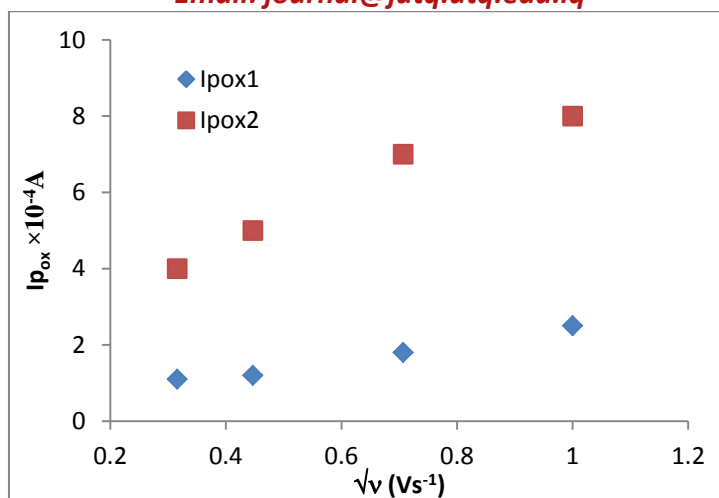


Figure (9): I_{pox1} and I_{pox2} peaks of oxidation versus $v^{1/2}$ for 0.1% doping of lignin resin

Figures (10-12) show a linear relationship between F_p with v for oxidation peaks to ratios (0.01,0.05,0.1)% proves that the system at fast rates of v suffers from quick electron transfer specially just after 1vs^{-1} before which a chemical reaction may happens, indicated by the sharp fall in the curve. Such behavior points out to the controlled diffusion process at the specified potentials [13, 14].

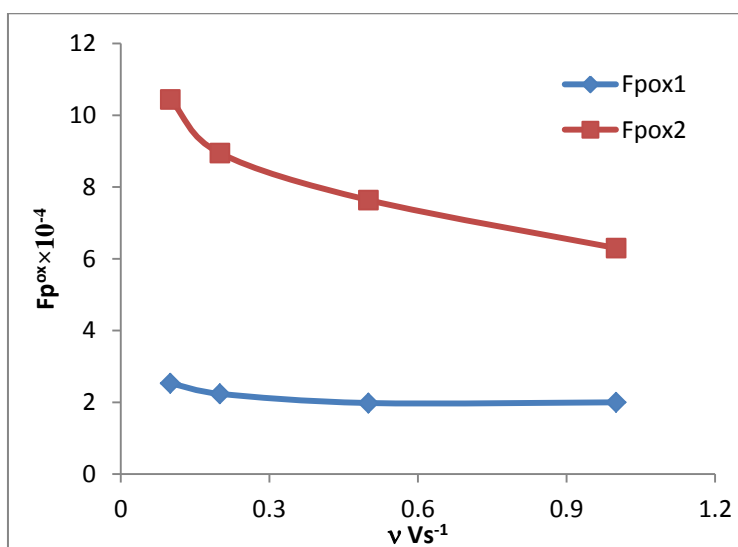


Figure (10): Current function Fp^{ox1} and Fp^{ox2} versus scan rate for 0.01% doping of lignin resin

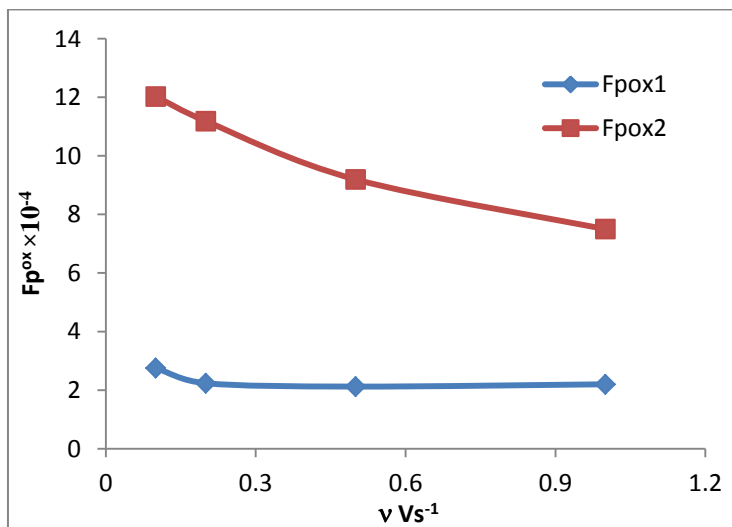


Figure (11): Current function Fp^{ox1} and Fp^{ox2} versus scan rate for 0.05% doping of lignin resin

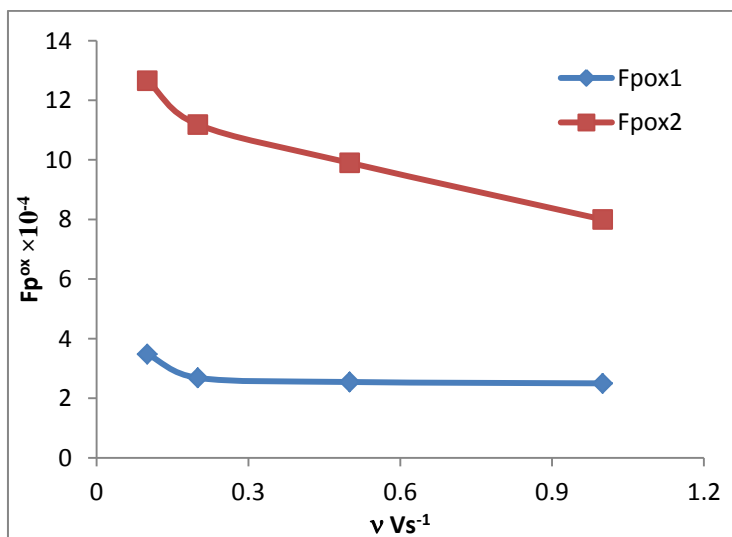


Figure (12): Current function Fp^{ox1} and Fp^{ox2} versus scan rate for 0.1% doping of lignin resin

Figures (13) and (14) show the cyclic voltammograms of (0.15 %) and (0.2%) respectively, doping of lignin at a potential range of 2 to -2.5 V at different scan rates. It is clear that oxidation peaks shifted to higher potentials as v increases in each case with decrease in values current at scan rats 0.5 Vs^{-1} to 1 Vs^{-1} . The overall results of cyclic voltommogram data of 0.15% and 0.2 % are given in Tables (5) and (6) respectively. A linear relationship is obtained between oxidation peaks as a function of v as shown in Figures (15) and (16) for 0.15 % and Figures (17) and (18) for 0.2 %, all exhibit the one electron transfer under a controlled diffusion processes. the broad oxidation peaks indicate the oxidation of both lignin and Rh B upon as v increases from 0.1 Vs^{-1} to 0.2 Vs^{-1} .

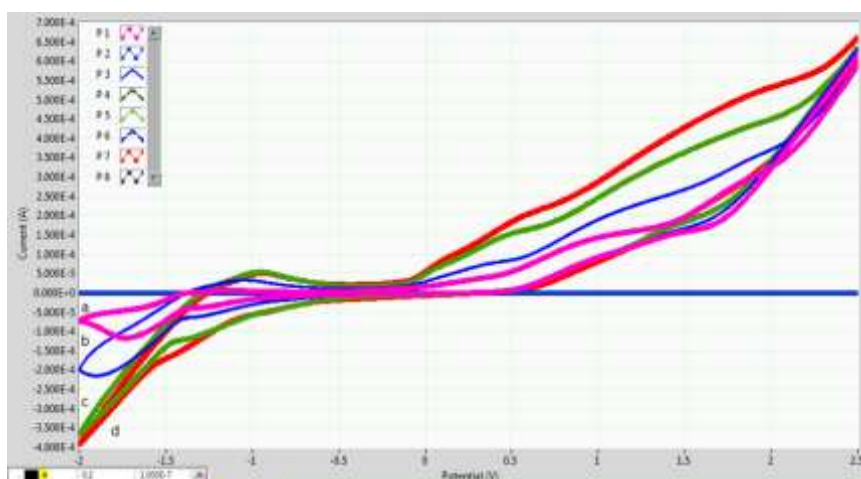


Figure (13): Cyclic voltammogram for 0.15 % doping of lignin resin at scan rates (a) 0.1 Vs^{-1} (b) 0.2 Vs^{-1} (c) 0.5 Vs^{-1} (d) 1 Vs^{-1}

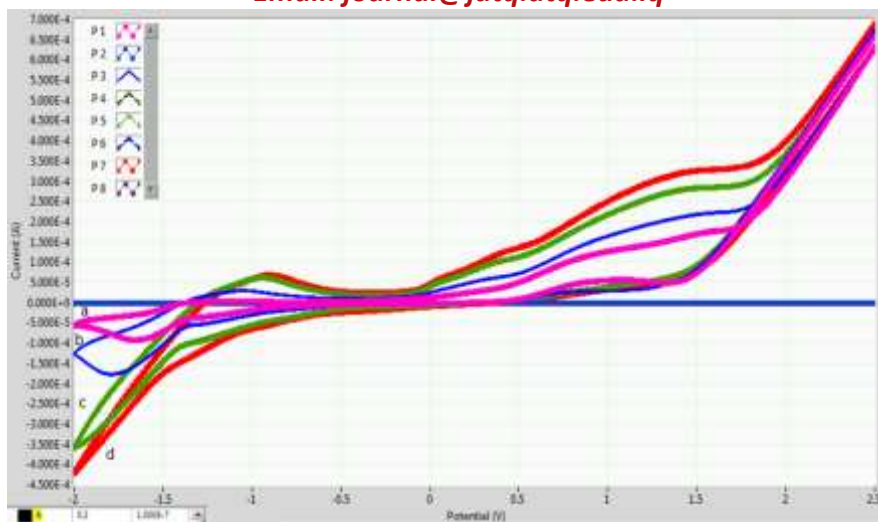


Figure (14): Cyclic voltammogram for 0.2 % doping of lignin resin at scan rates (a) 0.1Vs^{-1} (b) 0.2Vs^{-1} (c) 0.5Vs^{-1} (d) 1Vs^{-1}

Table (5): Cyclic Voltammogram data of 0.15% doping of lignin resin at different scan rates

ν $\text{V}\cdot\text{sec}^{-1}$	$\sqrt{\nu}$ $(\text{Vs}^{-1})^{1/2}$	$I_{p_{ox1}}$ A (10^{-5})	Fp^{ox1} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-5})	$I_{p_{ox2}}$ A (10^{-5})	Fp^{ox2} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-5})
0.1	0.316	1.7	5.379	2.75	8.702
0.2	0.447	2.1	4.697	3.5	7.829
0.5	0.707	1.5	2.121	4.5	6.364
1.00	1.000	2	2	5.5	5.5

Table (6): Cyclic Voltammogram data of 0.2% doping of lignin resin at different scan rates

ν $\text{V}\cdot\text{sec}^{-1}$	$\sqrt{\nu}$ $(\text{Vs}^{-1})^{1/2}$	$I_{p_{ox1}}$ A (10^{-5})	Fp^{ox1} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-5})	$I_{p_{ox2}}$ A (10^{-5})	Fp^{ox2} $\text{A}/(\text{V}\cdot\text{s}^{-1})^{1/2}$ (10^{-5})
0.1	0.316	1.5	4.746	1.8	5.696
0.2	0.447	1.7	3.803	2.3	5.145

0.5	0.707	1	1.414	3	4.243
1.00	1.000	1.4	1.4	3.5	3.5

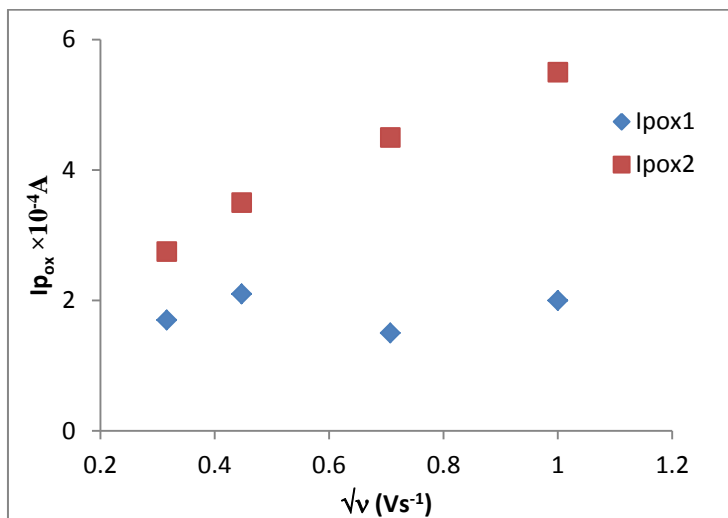


Figure (15): $I_{p^{ox1}}$ and $I_{p^{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.15% doping of lignin resin

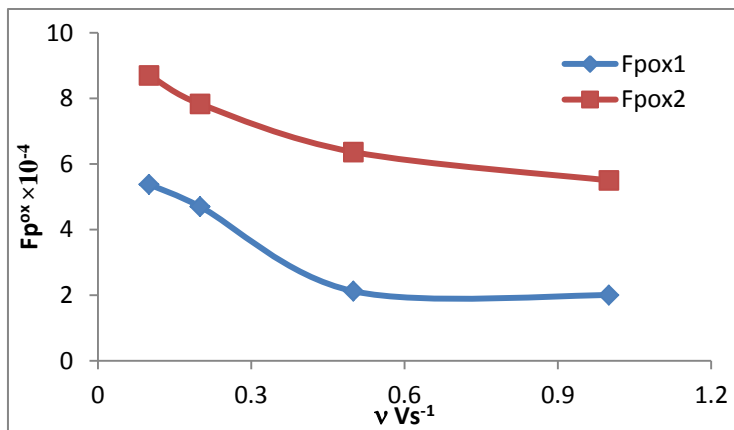


Figure (16): Current function $F_{p^{ox1}}$ and $F_{p^{ox2}}$ versus scan rate for 0.15 % doping of lignin resin

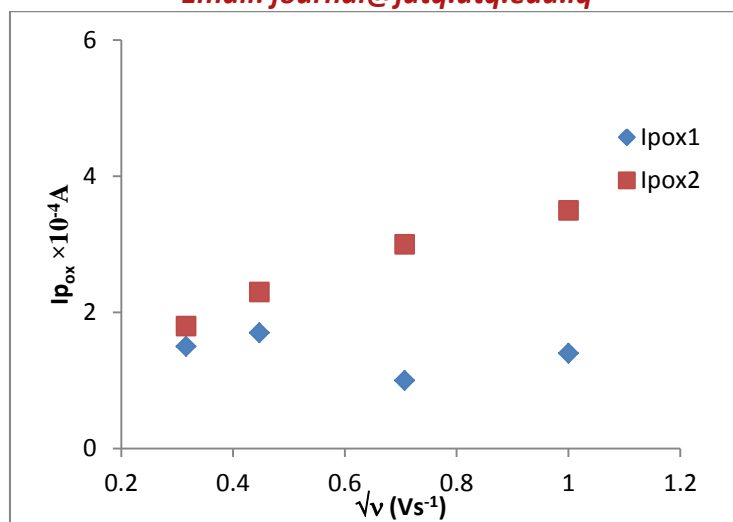


Figure (17): $I_{p^{ox1}}$ and $I_{p^{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.2% doping of lignin resin

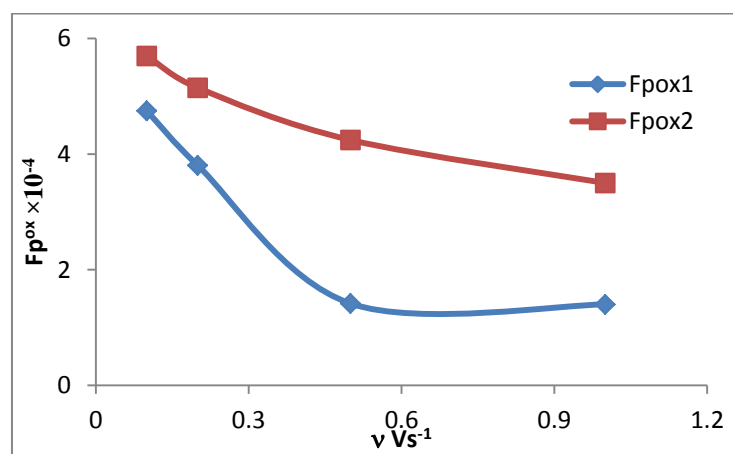


Figure (18): Current function $F_{p^{ox1}}$ and $F_{p^{ox2}}$ versus scan rate for 0.2% doping of lignin resin

The effect of the different percentages that have been used, it is concluded that 0.1 % is the best one among others, which is in accordance with the same result obtained during the electrical studies, Bulk conductivity in doped polymer material is limited by the need for the electrons to jump from one chain to the next, i.e., in molecular terms an intermolecular charge transfer

reaction. It is also limited by macroscopic factors such as bad contacts between different crystalline domains in the material [15].

Conclusion

In this study of cyclic voltammetry, the results of linear relationship between I_{red} with $v^{1/2}$ of all doped lignin resin with different ratios of Rhodamine B that the electron transfer was a process of one electron transfer.

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دراسة السلوك الكهروكيميائي لراتنج اللكنين المشوب بنسب مختلفة
بصبغة الرودامين ب
سماح حسين كاظم
قسم الكيمياء/ كلية العلوم/ جامعة ذي قار

الخلاصة

تضمن البحث دراسة السلوك الكهروكيميائي لراتنج اللكنين بوساطة تقنية المسح الجهدي الحلقي، وتم التركيز على خواصه المتوقعة بعد التشويب بصبغة الرودامين ب بنسب (0.01, 0.5, 0.1, 0.15, 0.2) % wt وذلك وفقا لما يسببه الانتقال الالكتروني بين الصبغة المشوبة وراتنج اللكنين حيث انعكس ايجابيا على ظهور واضح لقمم التأكسد والأختزال رافق ذلك زيادة في قيم التيار الكهربائي (Ip) لمدى تغيير الجهد الكهربائي المسلط اذ تفاوتت وفقا لاختلاف سرعة المسح الجهدي المطبقة والمتوقعة أصلا في هذه الحالات. ان نتائج العلاقة الخطية المستنبطة بين Ip والجذر التربيعي لسرعة المسح الجهدي $v^{1/2}$ دلت على أن الانتقال الالكتروني هو عملية أنتقال الكترون واحد.