

Evaluation of Kinetic and Thermodynamic Parameters of 1, 1'-Dibenzoylferrocene in Methanol by Cyclic Voltammetry

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ABSTRACT

The electrochemical Kinetic study of 1, 1'-Dibenzoylferrocene (DBF) at a platinum working electrode in 0.1 mol dm⁻³ NaClO₄ non aqueous medium has been studied by Cyclic voltammetry. The heterogeneous electron transfer rate constants (*k*_s) and the diffusion coefficients (*D*_o) of DBF were estimated at various temperatures (283 – 323 K) and at different scan rates (0.05 – 0.5 V s⁻¹). A calibration curve, linear over the range of 1x10⁻³ – 9x10⁻³ mol dm⁻³, was plotted at the scan rate of 0.25 Vs⁻¹. This plot can be used to analyze an unknown sample of the compound. The kinetic data was also used to evaluate the Activation energy (*E*_a). The thermodynamic parameters such as enthalpy change of activation (ΔH^*), Entropy change (ΔS^*) and Gibbs free energy change (ΔG^*) were also investigated during the study.

Keywords: 1,1'-dibenzoylferrocene (DBF), cyclic voltammetry, heterogeneous electron transfer rate constant (*k*_s) and the diffusion coefficient (*D*_o)

1. INTRODUCTION

Ferrocene is an organometallic compound having formula Fe (C₅H₅)₂. It has been attained the deep interest of the researchers toward its unusually stability and medicinal uses of its derivatives. Compounds of ferrocene such as Ferroquin and Hydroxy-Ferrocifen are used as an anti-malaria drug and for the Tamoxifen resistant breast cancer respectively. These products are also widely employed for other multiple purpose applications^{1, 2}. The industrial and medicinal importance of ferrocene and its derivatives are increasing day by day. For this purpose spectrochemical and electrochemical behavior of ferrocene moieties have been sought after. Ferrocene and its derivatives undergo reversible oxidation³. In benzoyl-substituted ferrocene an intramolecular charge transfer reaction takes place from the iron atom attached with the cyclopentadienyl ring where it is then delocalized over the carbonyl group conjugated to the cyclopentadienyl ring. In contrast with Ferrocene, 1, 1'-dibenzoylferrocene behave as the best photoinitiator.^{4, 6} It may decompose into free radicals and initiate the anionic polymerization when exposed to light. For this reason ferrocene and its derivatives has attracted attention in optical sensor technology and polymer science. Thermodynamic parameters along with kinetic aspect have also been reported for ferrocene and some of its derivatives.⁷⁻¹⁰ When ferrocene placed at the terminal positions in a molecule it may under go an electron transport process.^{8, 11} The solution photochemistry of benzoyl-substituted ferrocene has been investigated in substantial detail.^{12, 13}

Cyclic voltammetry is a very sophisticated and useful electrochemical technique which is commonly used to investigate the electrochemical behaviors of numerous compounds. The electrochemical behavior of ferrocene derivatives is usually characterized by a reversible voltammetric wave corresponding to the ferrocene/ferrocenium redox couple.¹⁴ Electrochemical behavior of Ferrocene and its derivatives has been studied at different electrode including platinum, glassy carbon, graphite and Gold electrode by different worker and researchers on the basis of their inertness.^{3, 4, 16} In our investigations Platinum working electrode has proved to be better option than others.

In the present work kinetic study of 1, 1'-dibenzoylferrocene has been pursued and the cyclic voltammetry has been employed towards this goal. To meet this objective 1, 1'-dibenzoylferrocene was electrochemically investigated by using platinum working electrode in non aqueous methanol system. 0.1 mol dm⁻³ NaClO₄ was used as an electrolyte. Effects of concentration of the product, Scan rate and temperature were studied as a function of Peak current *I*_p. The kinetic data was used to evaluate the Activation energy (*E*_a) and to calculate the thermodynamic parameters such as enthalpy change of activation (ΔH^*), Entropy change (ΔS^*) and Gibbs free energy change (ΔG^*).

2. EXPERIMENTAL

2.1 Chemicals

All the chemicals including ferrocene, benzoyl chloride, dichloromethane, anhydrous aluminum chloride, sodium chloride, ethanol, methanol, sodium per chlorate were of analytical grade (Merck or RDH). Deionized water was employed during synthesis of the product.

2.2 Synthesis and Characterization of 1, 1'-dibenzoyl ferrocene

The product, 1-1'-dibenzoyl ferrocene has been prepared, according to the previously reported method¹⁵, by acylation of ferrocene with benzoyl chloride in presence of anhydrous aluminum chloride. The product was recrystallized with ethanol. Due to highly photoinitiation nature of DBF all the reaction system was kept in dark. The structure characterization of synthesized derivative was carried out by using IR¹, HNMR¹³, CNMR and mass spectrometry.

The IR-Spectral study was carried out in the 4000-500 cm^{-1} in KBr disc. Only strong bands were considered for study. In this spectrum appearance of the strong bands at (1784.2, 1707.2, 1634.8, 1601.9) cm^{-1} may be assigned to the aromatic ketone part of the 1, 1'-dibenzoylferrocene, where as peaks at (3416.7, 1492.3, 1448.8, 1100.6, 999.7, 814.2 and 778.8) cm^{-1} may be ascribed to the ferrocene part of the complex as bands in these regions are observed in the spectrum of ferrocene. Mass spectrum of the synthesized complex confirms the formation of 1, 1'-dibenzoylferrocene. The m/e ratio of the complex found to be fit for 1, 1'-dibenzoylferrocene, i.e., $m/e = 394.24$. ^1H NMR spectrum of 1, 1'-dibenzoylferrocene shows intense signals on 4.58, 4.92, 7.43, 7.45, 7.52, 7.56, and 7.77 – 7.79 ppm. Thus the derivative was found to be 1, 1'-dibenzoylferrocene, having chemical formula $\text{C}_{24}\text{H}_{18}\text{FeO}_2$.

2.3 Instrumentation

CHI 660 C Electrochemical analyzer / work station is used to record the cyclic Voltammogram. A double walled glass cell with a volume of 20 ml connected with three electrodes, purged with nitrogen, has been employed for recording the electrochemical data. Platinum working electrode is used as anode, which was polished with 0.05 micron Gamma Alumina Powder and, rinsed with deionized water before each run, Ag/AgCl electrode is as reference electrode and a platinum wire provided the counter electrode.

Temperature of the system was altered by using Haake KT33 temperature bath connected to a double walled glass cell assembly.

2.4 Procedure

Stock solutions of 1-1'-dibenzoyl ferrocene of different concentrations 1.0×10^{-3} , 3.0×10^{-3} , 5.0×10^{-3} , 7.0×10^{-3} and 9.0×10^{-3} mol dm^{-3} were prepared which contained 0.1 mol dm^{-3} NaClO_4 in non aqueous methanol system. Since the compound is light sensitive therefore each time fresh solutions were prepared before every run. A known volume of each solution was placed in the double walled reaction cell connected with three electrode assembly. 0.1 mol dm^{-3} NaClO_4 is used as electrolyte in non aqueous alcoholic medium. All solutions were thoroughly flushed with high purity nitrogen for 20 min, to remove oxygen from solutions in the electrochemical cell. Effect of change in concentrations, of 1, 1'-dibenzoylferrocene, over peak current was monitored at different scan rates from $0.1 - 0.5 \text{ Vs}^{-1}$. The measurements for heterogeneous electron transfer rate constants (k_s), the diffusion coefficients (D_0) and the thermodynamic parameters of 1,1'-dibenzoylferrocene were carried out at different temperature from 283 – 323K.

3. RESULTS AND DISCUSSION

Electrochemical oxidation of 1, 1'-dibenzoylferrocene (DBF), at the three electrode assembly, with platinum as a reference electrode, in 0.1 mol dm^{-3} sodium per chlorate in methanol system have been studied by cyclic voltammetry (CV). Cyclic Voltammogram of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ DBF, in methanol systems. The peak potential of cathodic and anodic reaction were found to be around 0.4 to 0.3V, respectively. The detailed study of peak potential and their corresponding currents were observed at different sweep rate and temperatures Table-1.

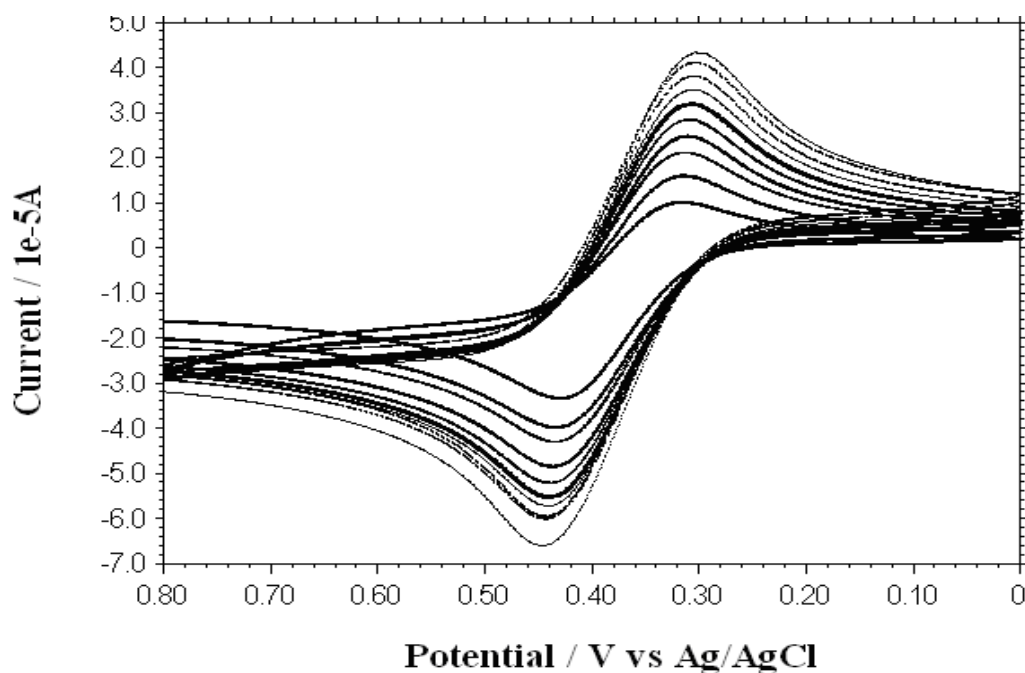


Fig-1: Cyclic Voltammogram of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ DBF in methanol (0.1 mol dm^{-3} NaClO_4 , 298 K) Pt vs Ag/AgCl electrode at different Scan rates ($0.05 - 0.5 \text{ Vs}^{-1}$)

Table-1: Scan rate (ν), anodic (E_{pa}) and cathodic (E_{pc}) peak potentials a anodic and cathodic current ratio (I_{pa}/I_{pc}), anodic and cathodic peak separation (ΔE_p) and half-wave potential($E_{1/2}$) for DBF in methanol

$\nu(V.s^{-1})$	$E_{pa}(V)$	$E_{pc}(V)$	$E_{1/2}(V)$	$E_{pa}-E_{pc}(V)$	I_{pc}/I_{pa}
283 K					
0.05	0.431	0.319	0.375	0.112	0.983
0.10	0.432	0.318	0.375	0.114	0.970
0.15	0.433	0.318	0.375	0.115	0.983
0.2	0.433	0.318	0.375	0.115	0.967
0.25	0.433	0.318	0.375	0.115	0.987
0.05	0.435	0.317	0.376	0.118	0.903
0.10	0.438	0.316	0.377	0.122	0.916
0.15	0.439	0.315	0.377	0.124	0.955
0.2	0.440	0.314	0.377	0.126	0.958
0.25	0.441	0.314	0.377	0.127	0.983
0.05	0.433	0.319	0.375	0.112	0.983
293 K					
0.05	0.434	0.324	0.379	0.110	1.513
0.10	0.434	0.323	0.378	0.111	1.003
0.15	0.435	0.323	0.379	0.112	1.339
0.20	0.435	0.322	0.378	0.113	1.019
0.25	0.435	0.322	0.378	0.113	1.066
0.30	0.437	0.320	0.378	0.117	1.286
0.35	0.439	0.318	0.378	0.121	1.064
0.40	0.439	0.316	0.377	0.123	1.062
0.45	0.440	0.315	0.377	0.125	1.071
0.50	0.442	0.315	0.378	0.127	1.000
303 K					
0.05	0.431	0.323	0.377	0.108	0.968
0.10	0.432	0.320	0.376	0.112	0.959
0.15	0.433	0.320	0.376	0.113	0.991
0.20	0.433	0.319	0.376	0.114	0.985
0.25	0.434	0.318	0.376	0.116	0.967
0.30	0.435	0.315	0.375	0.120	0.997
0.35	0.435	0.314	0.375	0.121	0.905
0.40	0.438	0.314	0.376	0.124	0.920
0.45	0.440	0.313	0.376	0.127	0.923
0.50	0.442	0.313	0.377	0.129	0.930
313 K					
0.05	0.434	0.325	0.379	0.109	0.942
0.10	0.435	0.325	0.38	0.11	0.939
0.15	0.436	0.324	0.38	0.112	0.949
0.20	0.436	0.323	0.379	0.113	0.929
0.25	0.437	0.321	0.379	0.116	0.950
0.30	0.438	0.321	0.379	0.117	0.981
0.35	0.439	0.320	0.379	0.119	0.988
0.40	0.443	0.320	0.381	0.123	0.954
0.45	0.444	0.319	0.381	0.125	0.986
0.50	0.445	0.313	0.379	0.132	0.974
323 K					
0.05	0.389	0.369	0.379	0.020	0.973
0.10	0.398	0.362	0.38	0.036	0.980
0.15	0.412	0.342	0.377	0.070	0.942
0.20	0.437	0.329	0.383	0.108	0.925
0.25	0.438	0.322	0.380	0.116	0.927
0.30	0.439	0.322	0.381	0.117	0.945
0.35	0.441	0.319	0.380	0.122	0.948
0.40	0.445	0.314	0.379	0.131	0.959
0.45	0.446	0.305	0.376	0.141	0.957
0.50	0.451	0.299	0.375	0.152	0.982

The I_{pa}/I_{pc} values of DBF in methanol systems are ≈ 1 and hence a reversible electron transfer reaction without any coupled chemical reaction.

For a reversible electron transfer process the no of electron calculated by the following equation¹⁶.

$$E_{\frac{p}{2}} - E_p = 2.2 \left(\frac{RT}{nF} \right)$$

Where E_p is the peak potential, $E_{p/2}$ the half peak potential at half value of the peak current, n is the number of electron involve in the process and F is the Fraday constant.

The curve obtained from the peak current I_p vs $v^{1/2}$ plot, has been used for calculating the values of diffusion coefficients for the complex i.e., 1, 1'- dibenzoylferrocene in non aqueous methanol the system.

The plots of anodic currents, I_{pa} versus the square root of the scan rate for DBF were linear which indicate that reactions are diffusion controlled, Figure-2.

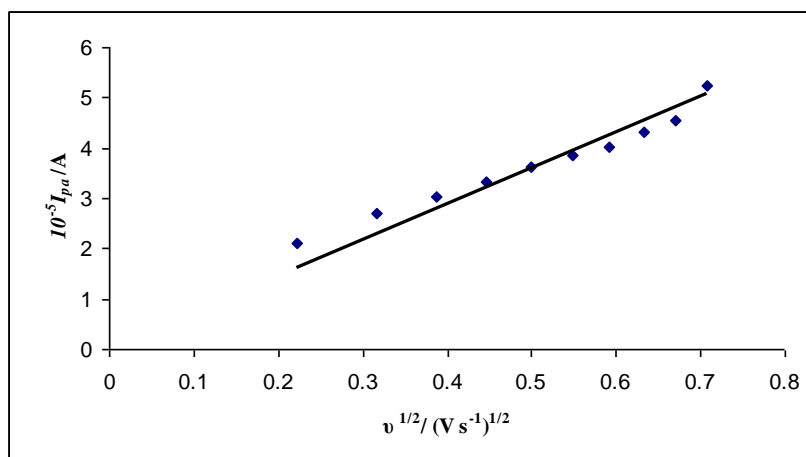


Fig-2: The plot of I_{pa} vs $v^{1/2}$ of 1.0×10^{-3} mol dm^{-3} DBF in methanol at 283 K

A comprehensive study was carried out to check the effect of change in concentration of DBF over Peak currents I_{pa} , at the scan rate of 0.05 V/s and at 298 K, which shows a linear trend over the concentration range of $1 \times 10^{-3} - 9 \times 10^{-3}$ mol dm^{-3} as shown in Figure-3. It shows that the procedure can be adopted to analyze an unknown concentration of DBF. Effect of change in concentration of DBF on Peak current I_{pa} in methanol is shown in Figure-3.

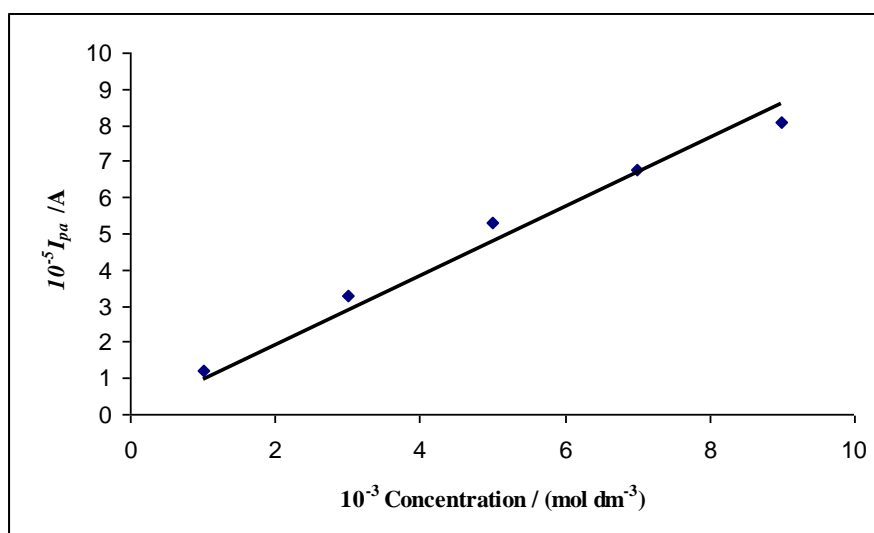


Fig-3: Plot of I_{pa} vs. the concentration of DBF in methanol, v : 0.05 V/s at 298 K.

As the values of anodic and cathodic peak potentials are slightly dependent on the scan rate therefore redox potentials for a couple is usually expressed as half wave potential $E_{1/2}$. The values of $E_{1/2}$ were found to be independent of change in scan rate. The half wave potential can be determined by using following relationship.¹⁷

$$E_{1/2} = E_{pa} - \frac{\Delta E_p}{2} \quad (1)$$

Where, E_{pa} is the anodic peak potential and ΔE_p is the difference between anodic and cathodic peak potentials. The values of $E_{1/2}$ almost constant within the given range of temperature. The peak separation values, ΔE_p values of DBF in methanol system is quasireversible as the ΔE_p are greater than 0.057V, as shown in Table-1.

It was also observed that separations between peaks potentials increase with the increase in scan rate, as shown in Figure-4, is the indication of charge transfer kinetics¹⁸⁻²⁰. The values for $E_{1/2}$ remain constant up to two decimal places; regardless of the scan rate one electron transfer process seems to be occurring in both the cases as potential is scanned in the anodic direction. The value of ratio I_{pc}/I_{pa} is almost constant with increase in scan rate as shown in Table-1. These values are approximately equal to 1, which shows the stability of the product and also suggest the single electron transfer reaction. In addition to that the anodic peak currents vary linearly with the square root of the scan rate as shown in Figure-2. These results lead to the conclusion that the dibenzoyl derivative of ferrocene oxidized quasi-reversibly from Fe (II) to Fe (III) at Platinum electrode.

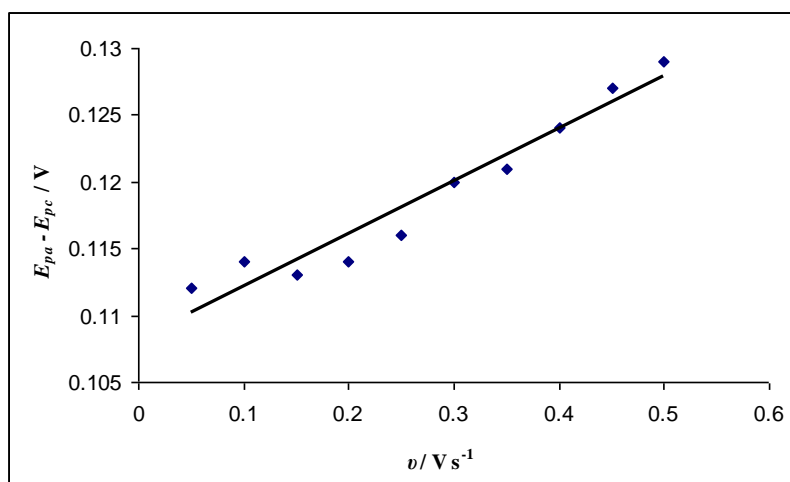


Fig-4: The plot of $E_{pa}-E_{pc}$ vs v of 1.0×10^{-3} mol dm^{-3} DBF in methanol at 303 K

The values of diffusion coefficients for the complex i.e., 1, 1'- dibenzoylferrocene (DBF), in methanol solutions were calculated using Randles- Sevcik equation²¹.

$$I_p = 0.4463(nF)^{3/2} (RT)^{-1/2} AC D_o^{1/2} v^{1/2}(2)$$

Where I_p is the peak current in amperes, n is the number of electron transferred in the reaction, F is the Faraday constant, R is the general gas constant, T is temperature in Kelvin, A is the surface area of the electrode (0.0314 cm^2 in this case), C is the concentration in mol dm^{-3} , D_o is the diffusion coefficient in ($\text{cm}^2 \text{ s}^{-1}$) and v is the scan rate in (Vs^{-1}).

Table-2: Effects of change in concentration of DBF over Peak currents I_{pa} at 298 K at the scan rate of 0.05 Vs^{-1} .

Concentration $\times 10^{-3}$ (mol dm^{-3})	$I_{pa} \times 10^{-5} \text{ A}$
1.0	1.214
3.0	3.301
5.0	5.304
7.0	6.752
9.0	8.091

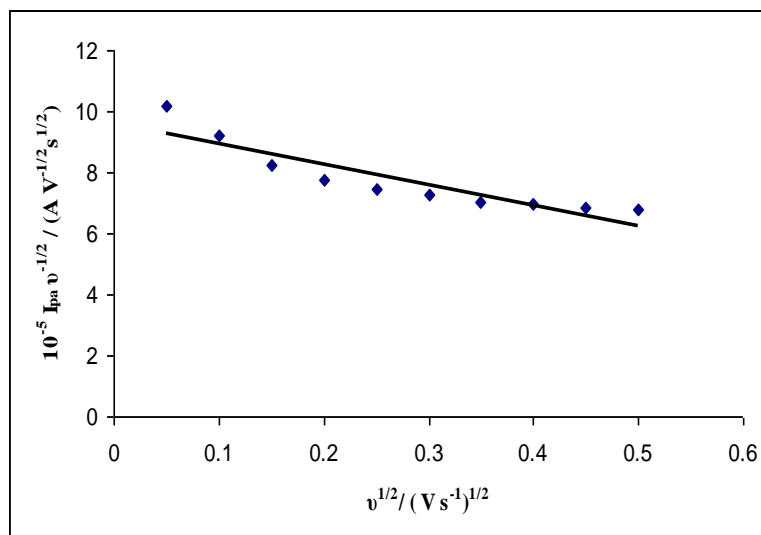


Fig-5: The plot of $I_{pa}/v^{1/2}$ vs. Scan rate of 1.0×10^{-3} mol dm^{-3} DBF in methanol at 303 K

The Value of Diffusion Coefficient D_o was evaluated by using the plot of I_{pa} vs $v^{1/2}$. These value were calculated for methanol systems of DBF and are reported in Table-3. Diffusion Coefficient D_o was found to increases with increase of temperature as the absolute viscosity of the solvent system decreases as shown in Figure-6.

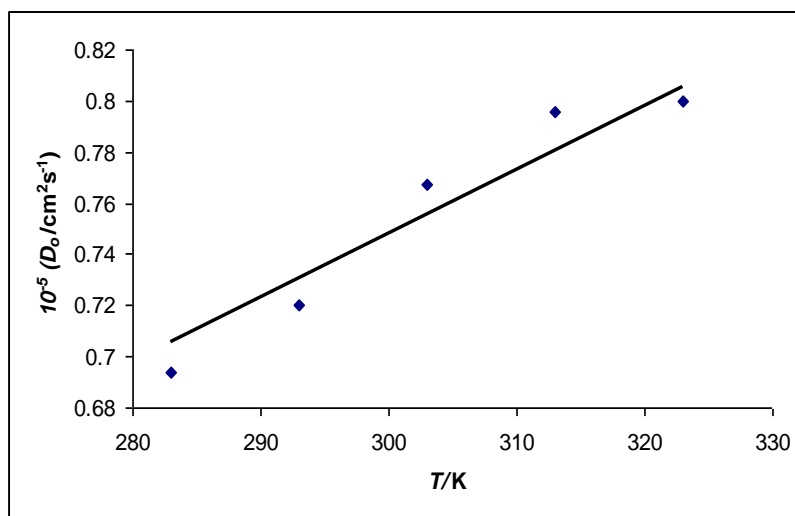


Fig-6: The plot of D_o of 1.0×10^{-3} mol dm^{-3} of DBF in methanol at different temperatures

Table-3: Summary of results pertaining to kinetic studies of DBF in methanol.

T (K)	$E_{1/2}$ (V)	D_o ($\times 10^{-5} \text{cm}^2 \text{s}^{-1}$)	k_s ($\times 10^{-3} \text{s}^{-1}$) At 0.25V/s
283	0.376	0.694	3.998
293	0.376	0.720	4.127
303	0.376	0.767	4.350
313	0.379	0.796	4.517
323	0.380	0.800	4.609

The values of Heterogenous Rate Constant (k_s) for the complex i.e., 1, 1'-dibenzoylferrocene (DBF), in non aqueous medium were calculated using Kochi equation²²:

$$k_s = 2.1 \left[\frac{\beta D_o n F V}{RT} \right]^{1/2} \exp \left[\frac{-\beta^2 n F}{RT} (E_{pa} - E_{pc}) \right] \quad (3)$$

Where I_p is the peak current (in Amperes, A), n is the total number of electron transferred in overall reaction, F is the Faraday's constant, A is the apparent surface area of the electrode (in cm^2), and C is the bulk concentration of the reactant (in mol cm^{-3}). Where β is a dimensionless parameter known as electron transfer coefficient, For quasireversible reaction it is usually practice approximate to 0.5²³. The n is the number of electron transferred in the reaction and D_o is the diffusion coefficient (in $\text{cm}^2 \text{s}^{-1}$), v is the scan rate in (V s^{-1}). E_{pa} is the peak potential of anodic peak and E_{pc} is the peak potential of the cathodic peak. The other parameters have their usual meanings.

Table-4: Summary of results pertaining to thermodynamic studies of DBF in methanol system.

ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	E_a (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})
1.601	-40.05	1.996	10.53

The effect of temperature on reaction kinetics was studied by using Arrhenius relation²⁴

$$\ln k = \ln A - \frac{E_a}{2.303RT} \quad (4)$$

Where E_a is energy of activation, R is general gas constant, A is the Arrhenius factor. The activation energy was evaluated from the slop of the plot of $\ln k$ vs $1/T$ as shown in Figure 7. The value of activation energy, of 1×10^{-3} M DBF, was found to be 24.445 K J/mol.

Thermodynamic parameters such as enthalpy change of activation ΔH^\ddagger and Entropy change ΔS^\ddagger were calculated by using heterogeneous rate constant data evaluated at different temperature, ²⁴⁻²⁶ as shown in Figure-8.

$$\ln\left(\frac{k_s}{z_{het}}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S^*}{R} \quad (5)$$

Where, Z_{het} is the collision number for heterogeneous electron transfer process and its value can be calculated by using the following relation²⁵⁻²⁷

$$Z_{het} = \left(-\frac{R}{2\pi M}\right)^{\frac{1}{2}} \quad (6)$$

The heterogeneous rate constant k_s increase with the temperature which shows that the oxidation of DBF is endothermic.

Negative value of entropy shows that reaction is non spontaneous. Gibbs free energy change (ΔG^*), for the oxidation of DBF in non aqueous methanol system, were calculated by using following relation ships:

$$\Delta G^* = \Delta H^* - 303\Delta S^* \quad (7)$$

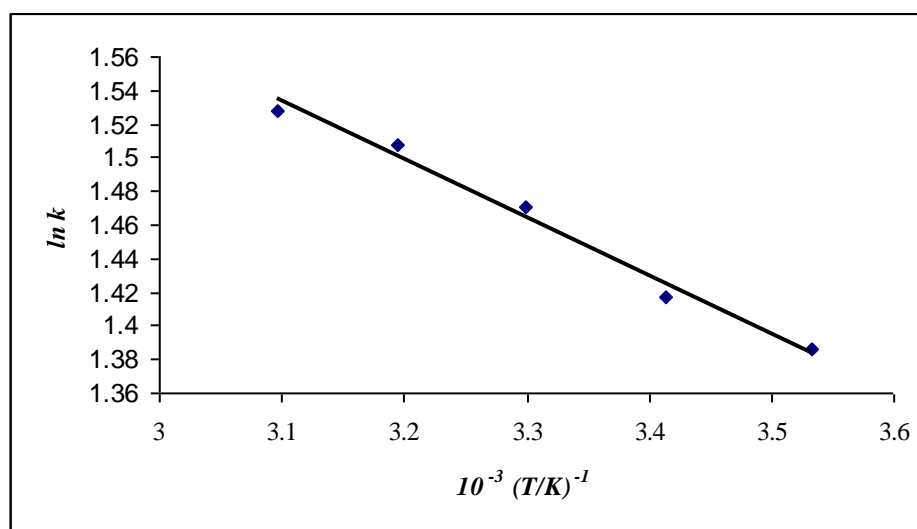


Fig-7: The plot of $1/T$ vs $\ln k$ of DBF in methanol for the evaluation of E_a for the oxidation of DBF in methanol system

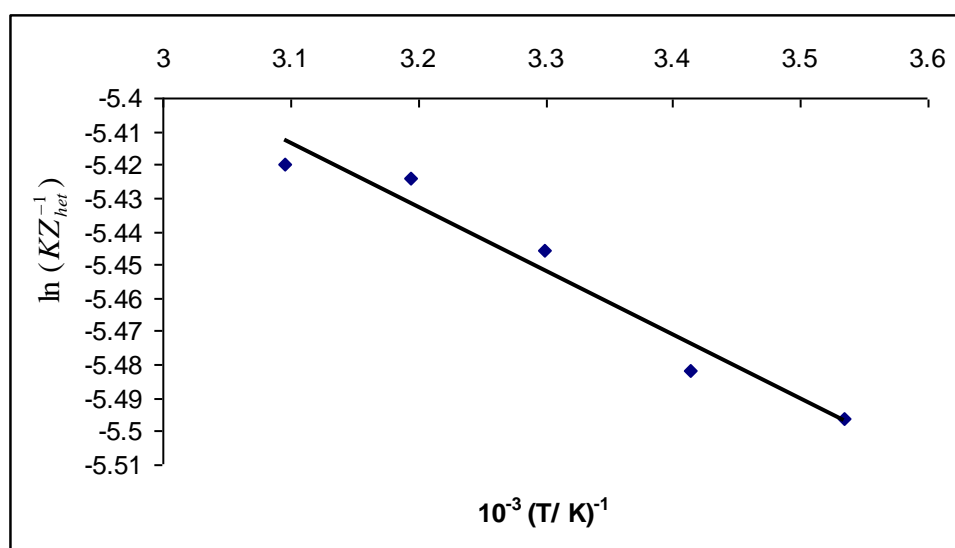


Fig-8: The plot of $1/T$ vs $\ln k$ of DBF in methanol for the evaluation of thermodynamic parameters for the oxidation of DBF in non aqueous methanol system.

4. CONCLUSIONS

The electrochemical oxidation of DBF has been carried out in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ non aqueous methanol solutions has been studied by cyclic voltammetry at different temperatures (283 – 323 K). DBF exhibits a quasireversible one electron transfer process over the whole temperature range. The reaction showed diffusion controlled process which is not coupled to any other reaction on this time scale. The diffusion coefficient of DBF showed linear dependence on temperature. The values of $E_{1/2}$ were found to be independent of change in scan rate. Thermodynamic parameters such

as Activation energy (E_a), enthalpy change of activation (ΔH^*), Entropy change (ΔS^*) and Gibbs free energy change (ΔG^*) indicated a non spontaneous process were also investigated during the study.

5. ACKNOWLEDGEMENT

We are thankful to Higher Education Commission (HEC) of Pakistan for providing us financial assistance.

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