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Using Cyclic Voltammetry, Potassium Ferricyanide Interaction with Crystal Violet in HNO_3 Medium

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Abstract: The cyclic voltammetry technique was used to study the electrochemical behavior of potassium ferricyanide and its interaction with crystal violet dye. The resulting voltammogram was analyzed for information about the redox reactions. The number of electrons involved in the redox reaction for a reversible process is related to the difference in peak potential by 59 mv/n (n is the number of electrons). The ratio of anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) for different concentrations of $K_3Fe\ (CN)\ _6$ was unity, indicating a reversible redox reaction. The mean peak potential difference (ΔE_p) for different potassium ferricyanide concentrations and also at different scan rates is very small, supporting the reversibility of the waves. The effects of different ligand crystal violet concentrations were studied on the potassium ferricyanide cyclic voltammogram with an increase in most solvation parameters. The stability constants and Gibbs free energies of the interaction between potassium ferricyanide and crystal violet were evaluated and support the complexation reaction.

keywords: Ferricyanide, redox reaction, crystal violet, stability constant, Gibbs free energy of complexation.

Highlights:

1. Discussing the redox reaction of potassium ferricyanide in the absence and presence of crystal violet dye,
2. Evaluating the thermodynamic parameters for the interaction of potassium ferricyanide with Crystal Violet in an HNO_3 medium at 300.45K.
3. catalytic appearance of hydrogen waves, which can be used in fuel cells.
4. appearance and catalytic effect of nitrate waves, which can be used in industry, especially military ones.

Facilities for the analytical estimation of the used materials by using cyclic voltammetry techniques

1.Introduction

The Fe (CN) 6 $^{3-}$ /Fe (CN) 6 $^{4-}$ redox couple is used as an electrochemical reversible redox system. $[Fe(CN)_6]^{3-}$ is made up of Fe^{3+} bonded in octahedral geometry (six cyanide ligands), and the iron is easily reduced to ferricyanide $[Fe(CN)_6]\ ^{4-}$ in which iron is Fe^{+2}. The redox couple is reversible, making or breaking Fe-C bonds.

In the ferrocyanide/ferricyanide redox couple is used for preparing Prussian blue, which is used as a chemical reducer in photographic techniques to remove silver from negatives and positives (dot etching). In the wire industry, potassium ferricyanide is used to precipitate copper. In histology, it is used to detect ferrous iron in biological tissues. This work aims to study the redox mechanism of potassium ferricyanide alone and in the presence of crystal violet dye and evaluate the different available thermodynamic functions [1-3].

2. Materials and methods

1.2. Reagents:

In deionized water, 0.1M $k_3Fe(CN)^6$ (provided by BDH CO.) was prepared, along with 0.1M crystal violet (Sigma Aldrich) dissolved in absolute ethyl alcohol and 0.1 M HNO3 (Al Gomheria Co.).

2.2. Instrumentation:

In the experimental part, a computer-controlled potentiostat, DY 2000, provided by the U.S.A., was used. A three-electrode glass cell was used with a glassy carbon electrode (3.0 mm), a standard silver/silver chloride electrode, and a platinum wire auxiliary electrode. The connections between the potentiostat and the cell are: black is the working electrode, white is the reference electrode, and red is the auxiliary electrode. All experiments were done at room temperature, 300.45K.

2.3. Procedure:

The glassy carbon electrode was polished well with emery paper doped with Al_2O_3 and alumina slurry on soft wool pads and rinsed well with distilled water before being used as a fresh glassy working electrode. N_2 was purged to make an oxygen-free solution.

3. Results and Discussion

Cyclic voltammetry of $k_3Fe(CN)_6$

The cyclic voltammetry for different concentrations of $K_3Fe(CN)_6$ was done in the window range of 1.2--1 V and 0.8--0.8 V.

The redox reaction of the electrochemical effect of $k_3Fe(CN)6$ exhibits three waves, one reduction wave at 0.22V and another reduction wave at 0.65V, as well as one oxidation peak at 0.35 V (see Fig 1). The first reduction was the reduction of $[Fe(CN)_{6]}.^{3-}$to $[Fe(CN)_{6]}^{4-}$ consuming one electron, and its reverse reaction is the opposite direction of the ferrocyanide to ferricyanide transformation.

The second reduction peak at -0.75 V is the hydrogen reduction wave [4] and shifted to less negative values on adding ferricyanide ions to facilitate the oxidation process.

Evaluation of the cyclic voltammetry Data:

Many equations are applied for the redox reaction [5-22].

$$i_p = 0.4463\, n^{3/2} F^{3/2} D^{1/2} AC/CRT^{1/2}\, v^{1/2} \quad (1)$$

$$D^{1/2} = (\text{slope, } i_p \text{ vs } v^{1/2}) \times (RT)^{1/2}/\ 0.4463\, n^{3/2} F^{1/2} AC \quad (2)$$

$$\Delta Ep = E_{pa} - E_{pc} = 2.303\, RT/nF \quad (3)$$

$$\Psi = \gamma \alpha k_s/\ (nF/RT\, \nu D_0)^{1/2}. \quad (4)$$

$$\gamma = (D_a/D_0)^{3/2} 5)$$

Where **α** is the charge transfer coefficient, **α**=0.5 for reversible processes, **Ψ** is the charge transfer parameter taken as one for better approximation, Dc is the cathodic diffusion coefficient, **F** is faraday's constant and **A** is the heterogeneous electron rate constant from the electrode to the solution was calculated using:

$$k_s = 2.18^*\ [D_C\, \alpha_{na}\, F\, \nu/RT]^{1/2} \times \exp\ [\alpha^2\, nF\, \Delta Ep/RT] \ \ldots\ldots \ (6)$$

The surface coverage of the working electrode was increased by an increase in metal ion concentrations [23-30]. The cathodic quantity of electricity Q_c and the anodic quantity of electricity Q_a can be calculated by applying the following equation:

$$Q_c = n\, FA\, \Gamma_c \ldots\ldots\ldots\ldots (7)$$

$$Q_a = n\, FA\, \Gamma_a \ldots\ldots\ldots\ldots (8)$$

The above parameters can be estimated for $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$couple of waves and the results are presented in table (1) and Fig (1) for the effect of different potassium ferricyanide concentrations in 0.1M HNO_3 at 300.45

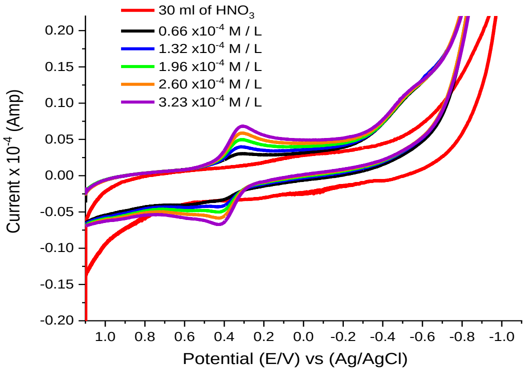

Fig (1): Effect of different concentrations of $K_3[Fe(CN_6)]$ in 30ml HNO_3 0.1M by using glassy carbon electrode at 300.45K and scan rate 0.1V. S^{-1}.

We observed from Table (1) the following:

- The difference in redox potential is very small, supporting the reversibility of the wave.
- I_{pc}/I_{pa} is equal unity, supporting the reversible mechanism.
- Because of an increase in the forward electron transfer reaction, the electron transfer rate constant increases with increasing potassium ferricyanide concentration until it reaches 1.96×10^{-4}M $Fe(CN)_6$.

- The electron transfers rate constant above the concentration of 1.96×10^{-4}M potassium ferricyanide is decreased, and that may facilitate the reverse reaction.

- The cathodic surface coverage $_{c}$ and the anodic surface coverage are largely affected by the increase in potassium ferricyanide concentration due mainly to the diffusion-controlled reactions.

- The cathodic quantity of electricity **Q_c** and the anodic one is slightly affected by increases in potassium ferricyanide concentrations due mainly to the molecular weight of potassium ferricyanide, which is very large.

- It was also observed in Fig. 1 that the hydrogen reduction wave appears at -0.6V, indicating its catalytic effect by both HNO_3 and potassium ferricyanide.

Table (1): Effect of different concentrations K_3 [Fe (CN_6)] in 30ml HNO_3 **0.1M** by using glassy carbon electrode at 300.45K and scan rate 0.1 V. S^{-1}.

[M] $\times 10^{-4}$mol.L^{-1}	**Ep,a Volt**	**Ep,c Volt**	**ΔEp Volt**	**(-) Ip,a$\times 10^{-6}$ Amp**	**Ip, c $\times 10^{-6}$ Amp**	**Ip,a/Ip,c**	**E° Volt**	**Da $\times 10^{-5}$ cm^2.s^{-1}**	**Dc $\times 10^{-5}$ cm^2.s^{-1}**	**Epc/2**	**αn_{ac}**	**k_sc $\times 10^{-2}$ cm.s^{-1}**	**Γc $\times 10^{-9}$ mol.cm^{-2}**	**(+) Qc $\times 10^{-6}$ Coulomb**	**Γ a $\times 10^{-10}$**	**(-) Qa $\times 10^{-6}$C**
0.66	0.402	0.335	0.067	0.79	0.64	1.23	0.368	2.01	1.32	0.397	0.76	2.62	0.21	0.66	2.71	0.82
1.32	0.397	0.329	0.067	2.03	1.92	1.05	0.363	3.33	2.98	0.394	0.74	3.87	0.65	1.99	6.93	2.10
1.96	0.391	0.320	0.070	2.18	3.19	0.68	0.355	1.73	3.71	0.390	0.68	4.29	1.09	3.30	7.45	2.26
2.60	0.389	0.318	0.070	3.71	3.44	1.08	0.353	2.86	2.46	0.388	0.68	3.48	1.17	3.56	12.6	3.85
3.23	0.387	0.311	0.075	4.39	4.49	0.97	0.349	2.59	2.71	0.383	0.66	3.79	1.53	4.65	15.0	4.55

- **Scan rate effect on redox reaction of potassium ferricyanide in 0.1M HNO_3at 300.45 K:**

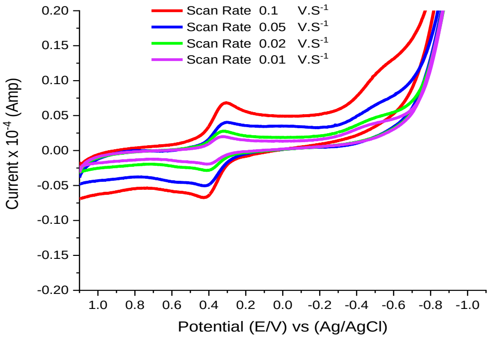

Fig.2. Effect of different scan rates of (3.23×10^{-4} M) $K_3[Fe(CN_6)]$ in 30ml HNO_3 **0**.1M by using glassy carbon electrode at 300.45K

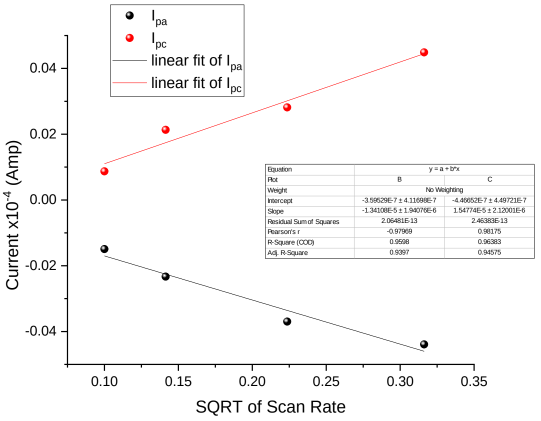

Fig (3): The relation between peak current and SQRT of scan rate of final addition of $K_3[Fe(CN_6)]$.

Table (2): Effect of different scan rates of (3.23×10^{-4} M) K_3 $Fe(CN_6)]$ in 30ml HNO_3 0.1M by using glassy carbon electrode at 300.45K.

ν v/s	**Ep,a Volt**	**Ep,c Volt**	**ΔEp Volt**	**(-)Ip,a $\times 10^{-6}$ Amp**	**Ip,c $\times 10^{-6}$ Amp**	**Ip,a/Ip,c**	**E° Volt**	**Da$\times 10^{-5}$ cm^2.s^{-1}**	**Dc $\times 10^{-5}$ cm^2/s**	**Epc/2**	**αn_a**	**k_{sc} $\times 10^{-2}$ cm.sec^{-1}**	**Γ c $\times 10^{-9}$ mol/cm^2**	**(+)Qc $\times$ 10^{-6}C**	**Γa$\times 10^{-9}$ mol.cm^{-2}**	**(-) Qa $\times 10^{-5}$C**
0.1	0.38	0.31	0.075	4.39	4.49	0.97	0.349	2.60	2.71	0.383	0.66	3.79	1.53	4.65	1.50	0.45
0.05	0.40	0.32	0.075	3.70	2.81	1.31	0.366	3.68	2.13	0.386	0.83	2.66	1.92	5.83	2.52	0.76
0.02	0.42	0.33	0.090	2.33	2.13	1.09	0.380	3.66	3.06	0.395	0.78	2.26	3.64	11.0	3.98	1.21
0.01	0.43	0.34	0.090	1.49	0.87	1.71	0.390	3.01	1.02	0.398	0.88	0.98	2.97	9.03	5.10	1.55

The effect of different scan rates,0.01,0.02,0.05,0.1v/sec was studied on 3.23×10^{-4}M $k_3Fe\ (CN)_6$ in 0.1 M HNO_3 and at 300.45k, and the evaluated data are shown in table (2) we noticed the following:

The effect of different scan rates of 0.01, 0.02, 0.05, 0.1v/sec was studied on 3.2310^{-4}M $k_3Fe\ (CN)_6$ in 0.1 M HNO_3 and at 300.45k, and the evaluated data are shown in table (2). We noticed the following:

1-**Δ**Ep is still very small, supporting the reversibility of the redox Fe $(CN)_6$ waves.

2-I_{pc}/ I_{pa} is increased by a decrease in the scan rate till it reaches 1.71 at 0.01 v/sec, indicating a more anodic reaction to proceed than the cathodic one.

3-the electron rate constant transfer $\mathbf{k_s}$ is slightly decreased by the decrease in scan rate supporting the kinetic diffusion mechanism.

4-the anodic and cathodic surface coverage, anodic and cathodic quantities of electricity are slightly affected by the decrease in scan rate, formulating the reversibility of redox waves.

Cyclic voltammetry of potassium ferricyanide with crystal violet dye in 0.1M HNO3, with different ligand crystal violet dye concentrations:

We observed from Fig. (4) that on increasing the addition of Crystal Violet the hydrogen wave appeared at -0.6 to -0.8 is shifted to more positive values and have the range -0.4 to -0.5V

due to its catalytic oxidation by the used crystal violet [31]

$H_2O + e^- \rightarrow 1/2H_{2\,(g)} + OH^-$ at -0.8V (1)

We noticed also that by more addition of crystal violet nitrate wave was observed at approximately -0.3V. This wave can be catalytically affected by the crystal violet concentration accelerating the two given equations as [32]:

$NO_3^- + H^+ + e^- \rightarrow 1/2N_2H_4 + H_2O$ (2)

$N_2H_4 + H^+ + e^- \rightarrow N_2H_5^+$ (3)

On using the crystal violet dye in the presence of potassium ferrocyanide catalytically, the hydrogen and nitrate waves were easily reduced, which can be applied in industry.

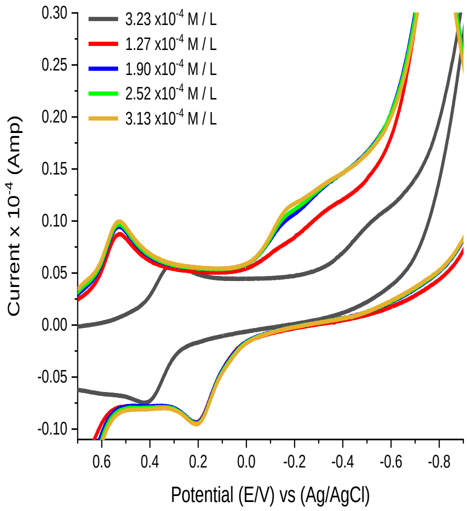

Fig (4): Effect of different concentrations of Crystal Violet dye in 1ml of $K_3[Fe(CN_6)]$ 0.01M and 30 ml of HNO_3 0.1M by using glassy carbon electrode at 300.45K and scan rate 0.1 V. S^{-1}.

Table (3): Effect of different concentrations of crystal violet dye in 1ml of $K_3[Fe(CN_6)]$ 0.01M and 30 ml of HNO_3 0.1M by using glassy carbon electrode at 300.45K and scan rate 0.1 V. S^{-1}

[M] x10^{-4} mol.L^{-1}	**[L] x10^{-4} mol.L^{-1}**	**Ep,a Volt**	**Ep,c Volt**	**ΔEp Volt**	**(-) Ip,a x10^{-6} Amp**	**Ip,c x10^{-6} Amp**	**Ip,a/Ip,c**	**E° Volt**	**Da x10^{-5} $cm^2.s^{-1}$**	**Dc x10^{-5} $cm^2.s^{-1}$**	**Epc/2**	**αnac**	**kscx10^{-2} $cm.s^{-1}$**	**Γc x10^{-9} $mol.cm^{-2}$**	**(+) Qc x 10^{-6} C**	**Γ a x10^{-9} $mol.cm^{-2}$**	**(-) Qax 10^{-6} C**
3.18	1.27	0.43	0.339	0.094	5.65	6.32	0.892	0.386	4.40	5.53	0.412	0.652	6.41	2.16	6.55	1.92	5.85
3.16	1.90	0.42	0.335	0.086	5.98	6.69	0.895	0.379	5.01	6.25	0.410	0.640	6.27	2.28	6.92	2.04	6.20
3.14	2.52	0.41	0.334	0.082	6.00	6.75	0.889	0.375	5.10	6.45	0.408	0.644	6.14	2.30	6.99	2.05	6.21
3.13	3.13	0.40	0.330	0.075	6.15	7.00	0.878	0.368	5.43	7.04	0.406	0.633	5.94	2.39	7.25	2.10	6.37

From table (3), we noticed the following:

- ΔEp, the difference in electrochemical potential is small, indicating no change in the reversibility of redox waves.
- I_{pc}/I_{pa} values are less than 1 for crystal violet (C.V) potassium ferricyanide, indicating less reversibility in comparison to that in the absence of C.V.

- **The potassium ferricyanide cyclic voltammogram has nearly constant values, indicating that crystal violet additions have the same effect as the potassium ferricyanide cyclic voltammogram.**
- A little increase in **D_c, D_a** by adding crystal violet to potassium ferricyanide.
- little increase in solvation parameters for **k_s, Q_c, Q_a**, by adding crystal violet to potassium ferricyanide.

We noticed from Fig. 4 that there is a shift in the ferricyanide reduction wave and hydrogen wave to less value on adding crystal violet, indicating the end of reduction (catalytically) by adding crystal violet.

The oxidation peak of the ferricyanide ion is also shifted to a less positive potential, facilitating its appearance catalytically.

Effects of different scan rates were studied at different scans for crystal violet plus potassium ferricyanide:

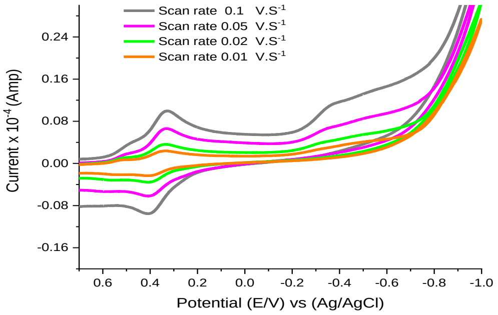

Fig (5): Effect of different scan rates of (3.13 x 10^{-4} M) of crystal violet dye in 1ml of $K_3[Fe(CN_6)]$ 0.01M and 30 ml of HNO_3 0.1M by using glassy carbon electrode at 300.45K

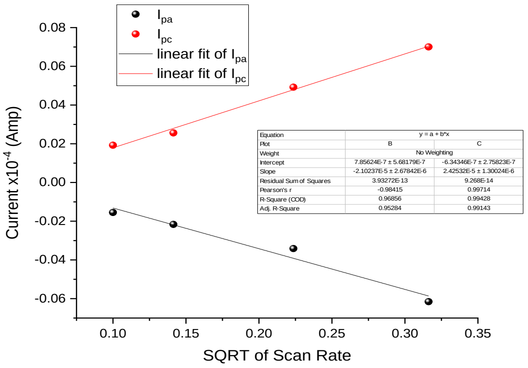

Fig (6): The relation between peak current and SQRT of scan rate of complex

Table (4): Effect of different scan rates of (3.13 x 10^{-4} M) of crystal violet dye in 1ml of $K_3[Fe(CN_6)]$ 0.01M and 30 ml of HNO_3 0.1M by using glassy carbon electrode at 300.45K

ν $V.S^{-1}$	**Ep,a Volt**	**Ep,c Volt**	**ΔEp Volt**	**(-)Ip,a x10^{-6} Amp**	**Ip,c x10^{-6} Amp**	**Ip,a/Ip,c**	**E° Volt**	**Da x10^{-5} $cm^2.s^{-1}$**	**Dc x10^{-5} $cm^2.s^{-1}$**	**Epc/2**	**αna**	**ksc x10^{-2}**	**Γ c x10^{-9} $mol.cm^{-2}$**	**(+)Qc x 10^{-5}C**	**Γa x10^{-9} $mol.cm^{-2}$**	**(-) Qa x 10^{-5}C**
0.1	0.406	0.330	0.075	6.15	7.00	0.87	0.368	5.43	7.03	0.406	0.63	5.94	2.39	0.72	2.10	0.63
0.05	0.409	0.339	0.070	3.41	4.92	0.69	0.374	3.34	6.95	0.409	0.68	4.12	3.36	1.02	2.33	0.70
0.02	0.410	0.344	0.065	2.16	2.56	0.84	0.377	3.36	4.70	0.412	0.69	2.08	4.37	1.33	3.69	1.12
0.01	0.412	0.357	0.054	1.55	1.92	0.80	0.385	3.45	5.31	0.415	0.84	1.54	6.57	1.99	5.30	1.61

Table (5): Stability constant for ($K_3[Fe(CN_6)]$ _ Crystal Violet) complex in 30 ml of HNO_3 0.1M by using glassy carbon electrode at 300.45K and scan rate 0.1 V. S^{-1} (n = 1).

[M] x10^{-4} $mol.L^{-1}$	**[L] x10^{-4} $mol.L^{-1}$**	**(Ep,a)M**	**(Ep,a)C**	**ΔE v**	**J**	**Log[L]**	**Log βj**	**Bj**	**ΔG (J/mol)**	**ΔG (KJ/mol)**
3.18	1.27	0.3492	0.3862	-0.037	0.4	-6.8948	2.137	137.19	-12295.6	-12.2952
3.16	1.90	0.3492	0.3792	-0.0299	0.6	-6.7215	3.530	3388.4	-20307.2	-20.3072
3.14	2.52	0.3492	0.3755	-0.0262	0.8	-6.5993	4.839	69063.6	-27839.0	-27.8390
3.13	3.13	0.3492	0.3682	-0.0189	1	-6.5051	6.187	1540346.4	-35595.8	-35.5958

Table (6): Effect of scan rate on stability constant of ($K_3[Fe(CN_6)]$ _ Crystal Violet) complex in 30 ml of HNO_3 $_0$.1M by using glassy carbon electrode at 300.45K and scan rate 0.1 V. S^{-1} (n = 1)

υ	**(Ep,a)M**	**(Ep,a)C**	**ΔE v**	**J**	**Log[L]**	**Log βj**	**βj**	**ΔG (J/mol)**	**ΔG (KJ/mol)**
0.1	0.349	0.368	-0.0189	1	-6.50515	6.1876	1540346.486	-35595.88	-35.5958
0.05	0.366	0.374	-0.0079	1	-6.50515	6.3716	2352907.527	-36654.31	-36.6543
0.02	0.380	0.377	0.00284	1	-6.50515	6.5529	3571969.63	-37697.3	-37.6972
0.01	0.390	0.385	0.00475	1	-6.50515	6.5849	3845704.928	-37881.78	-37.8817

The effects of different scan rates were studied at different scans for crystal violet plus potassium ferricyanide. decrease in Ep, I_{pc}/I_{pa}, Dc, and Da with increasing crystal violet concentration, indicating complex reaction; increase in k_s, Q_c, Q_a, values with decreasing scan rate, proving redox reaction diffusibility.

Current vs. scan rate straight-line relationships Fig. 6: A diffusion-reaction was observed.

The thermodynamic parameters, stability constant, and Gibbs free energy of interaction for crystal violet with potassium ferricyanide were evaluated as explained in previous works, and their values were cited in tables (5) and (6) for scan rate effect.

The thermodynamic functions proved that the complexation of the reaction of crystal violet with potassium ferricyanide is a type of strong physical interaction.

Conclusions

1. The number of electrons in the electrode process is one.
2. The peak potential difference for $Fe(CN)_6{}^{3-}$ ion is one, indicating that the redox reaction is reversible.
3. I_{pc}/I_{pa} is unity for $Fe(CN)_6{}^{3-}$ ion redox mechanisms that support the reversible mechanism.
4. In the presence of crystal violet, Ep is still small, indicating the reversibility mechanism.
5. In crystal violet and ferricyanide ions, $\boldsymbol{\alpha}_{\mathbf{na}}$ values are constant, indicating the same mechanism.
6. A small increase in k_s, Q_c, Q_a, D_a, and D_c values on adding crystal violet to ferricyanide ions indicates small complexation.
7. The thermodynamic parameters, stability constants, and Gibbs free energy of complexation for the interaction of crystal violet with ferricyanide ions are moderate values, indicating complexation with strong physical interaction.

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