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Cyclic voltammetry of the oxidation of potassium permanganate using succinic acid

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Abstract

Redox reaction for potassium permanganate in absence and presence of succinic acid was studied by using cyclic voltammetry in 0.1 KCl as supporting electrolyte. Glassy carbon electrode was used as working electrode, whereas the other two electrodes are Ag/AgCl/sat. KCl, reference electrode and platinum wire auxiliary electrode. The oxidation stability constants and Gibbs free energies of oxidation were evaluated, and their data were discussed.

Key words: Cyclic voltammetry, oxidation of potassium permanganate, stability constant, Gibbs free energies of oxidation

1. Introduction

Cyclic voltammetry (CV) is an electrochemical technique used to measure the change of the electrode potential and the current flow of solution of analysts. Cyclic voltammetry (CV) is commonly used for the determination of the stability of the products of the reaction, study the kinetics of electron transfer, characterization of the redox system and redox mechanism of organometallic compounds [1-4]. Potassium permanganate is very strong oxidizing agent, it is an intense dark purple color. Its reduction to Mn^{2+} , the solution will be changed to faint pink color. The net five electrons reduction of Mn (VII) to Mn (II), reaction and the final products of the redox reaction depends on the nature of the reductants and reaction conditions [5-13]. KMnO₄ can be used to oxidize many organic compounds. The products obtained can be depending on the condition and the final products are often carboxylic acids [6]. Discussion the effect of oxidation of carboxylic acid by potassium permanganate is necessary for analytical titrations.

The aim of this concerning the redox reaction of potassium permanganate in absence and presence of succinic acid by using cyclic voltammetry in 0.1 KCl. Glassy carbon electrode was used as working electrode, whereas the other two electrodes are Ag/AgCl/sat KCl, reference electrode and platinum wire auxiliary electrode. The oxidation stability constants and Gibbs free energies of oxidation were evaluated, and their data were discussed.

2. Experimental

The chemicals used potassium permanganate (KMnO₄), succinic acid and potassium chloride (KCl) was provided from Sigma Aldrich Co. Bidestilled water with conductivity 2.5 micro ohm⁻¹ was used. Cyclic voltammetry instrument of DY 2000 potentiostate was used for cyclic voltammograms developing at different scan rates. Pure N2 gas was passed for 10 minutes in each solution to ensure the removing of dissolved oxygen in solutions.

Three electrodes system were used, the first electrode is the glassy carbon electrode (GCE) as working electrode, and the second electrode is Ag/AgCl reference electrode filled with saturated KCl. The third electrode is platinum wire as auxiliary electrode.

3. Results and Discussion

3.1. Cyclic voltammetry of KMnO₄

The cyclic voltammograms (CV) for redox behavior of KMnO₄ in 0.1 KCl solution as supporting electrolyte was studied in the range from 1 Volt (V) to -1 V. The reduction proceeded, whereas the oxidation took place in the range of -1 V to 1 V. voltammograms in Fig. (1) show four reduction waves and one oxidation peak.

The suggested mechanisms for the reduction waves are: $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$ (1)

At approximately ~ 0.5 V which has very small peak.

After wards the following reaction proceeds to form more manganese oxides at ~ 0.3 Volt.

 $MnO_4^{2-} + 2H_2O + 2e^- \rightleftharpoons MnO_2$ (2)

Further reduction follows the following equation at ~ 0.002 V:

 $3Mn_3O_4(S) + 4H_2O + 2e^- \rightleftharpoons 2Mn_3O_4(S) + OH^-(3)$

Peak (I) at ~ - 0.35 V illustrated in Fig. (1) Follows the reaction:

 $Mn_3O_4(S) + 4H_2O + 2e^- \rightleftharpoons 3Mn(OH)_2(S) + 2OH^-(4)$ Whereas the oxidation peak proceeds at approximately 0.3 V through the following reaction:

Peak (II) at ~ 0.27 V illustrated in the Fig. (1): $3Mn(OH)_2(S) + 2OH^- \rightleftharpoons Mn_3O_4(S) + 4H_2O + 2e^-(5)$ Many concentrations of KMnO₄ were used ranging from 6.25*10⁻⁶ N to 1.67*10⁻⁵ N in 0.1 KCl at 16.7 °C .

Analysis of peaks (I) and (II) couple in Fig.1

The equations used for the electrochemical voltammetry calculations for couple of peaks (I) & (II) are explained and illustrated in the following equations:

(6)

Surface coverage which is the electrode surface covered by electro active species is calculated using equation [14-19]:

$$\Gamma = I_P \quad 4RT / n^2 F^2 A V$$

where is Γ is the surface coverage , R is the universal gas constant , F is Faraday constant 96485 C. mol⁻¹, A is the surface area of the electrode in cm², n is the number of electrons in the redox reactions, V is the scan rate (V.S⁻¹), T is the absolute temperature , I_P is the current in ampere.

The quantity of electricity consumed during redox reaction can be calculated using equation [6-11]:

 $Q = n F A \Gamma$ (7) Diffusion coefficient was calculated by using Randdless Seveik equation [15 – 16]:

 $I_{\rm P} = (2.69*10^{-5}) \ n^{3/2} \ A \ D^{1/2} \ V^{1/2} \ C$ (8)

where I_P is the current in ampere, A is the surface area of the working electrode, D is the diffusion coefficient in cm³/sec. V is the scan rate (V/S) and C is the concentration of KMnO₄.

 ΔEp is the difference between anodic and cathodic peak potentials.

 $\Delta E p = E_{Pa} - E_{Pc} \tag{9}$

The heterogeneous electron rate constant (k_s) can be calculated by applying equation [20 - 25]:

 $k_s=2.18(D\alpha n_aFV/RT)^{1/2}\exp\{\alpha^2 nF/RT(E_{Pc}-E_{Pa})\}$ (10)

where α is the charge transfer coefficient, n_a is the number of electrons involved in the redox processes and αn_a can be calculated from the equation:

$$(E_{Pc}-E_{Pc}/2)=(1.857RT/\alpha n_{a}F)$$
 (11)
where $E_{Pc}/2$ is the half peak potential and α equal 0.5

where $E_{Pc}/2$ is the half peak potential and α equal 0.5 as approximation for quasi reversible system.

The above parameters were calculated for the anodic and cathodic behavior for the couple reaction chosen for peaks

(I) & (II). The evaluated parameters are calculated and tabulated in Table (1) for the couple of peaks (I) & (II) of both the anodic peak (a) and cathodic peak (c).

The evaluated parameters E_{Pa} is anodic wave potential , I_{Pa} is anodic peak current , D_a is anodic diffusion coefficient , k_s is electron rate constant, Γ_a is anodic surface coverage , Q_a is anodic quantity of electricity for the anodic peak (II) which are increased with increase of KMnO₄ concentration in 0.1 M KCl (see Table(1) and Fig. (1). Also, the same parameters evaluated for cathodic peak are increased by increase of KMnO₄ concentration favoring more diffusion.

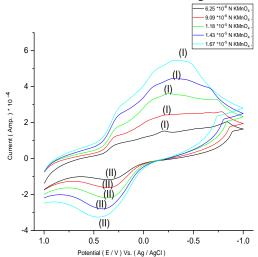


Fig. (1): Voltammograms of different concentrations of 0.1 N KMnO₄ in 0.1 M KCl as supporting electrolyte at 16.7 $^{\circ}$ C using glassy carbon (GCE).

Table (1): Cyclic voltammetric and kinetic parameters (D_a , D_c , k_s , Γ_a , Γ_c , Q_a and Q_c) of reduction peak couples (I) and oxidation peak couples (II) for different concentrations of KMnO₄ in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode.

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[M]x10 ⁵ mol.eqv./lit	Ep _a (volt)	Ep _c (volt)	ΔEp (volt)	Ip _a /Ip _c	E° (volt)	$\begin{array}{c} \text{Da} \\ \text{x10}^6 \\ \text{cm}^3/\text{sec.} \end{array}$	$\begin{array}{c} Dc \\ x10^6 \\ cm^3/sec. \end{array}$	Ep _{c/2} (volt)	αn _a	k _s x10 ⁻² cm/sec.	$\frac{\Gamma_c}{x10^8} \\ mol/cm^2$	$(+) Q_{c} Q_{c} X 10^{4} C$	$\begin{array}{c} \Gamma_a \\ x10^8 \\ mol/cm^2 \end{array}$	(-) Q _a x10 ⁴ C
0.625	0.323	-0.188	0.511	0.815	0.0675	1.08	1.62	-0.030	0.294	0.833	0.501	0.304	0.409	0.248
0.909	0.331	-0.216	0.547	0.617	0.0575	1.74	4.57	0.083	0.155	2.09	1.23	0.743	0.757	0.458
1.18	0.352	-0.219	0.571	0.681	0.0665	2.53	5.44	0.093	0.171	3.87	1.73	1.05	1.18	0.715
1.43	0.383	-0.279	0.662	0.775	0.0520	3.09	5.16	0.099	0.146	21.6	2.05	1.24	1.59	0.962
1.67	0.429	-0.318	0.747	0.692	0.0555	3.10	6.48	0.109	0.108	114	2.68	1.62	1.85	1.12

Scan rate effect on the redox reaction of KMnO₄

The different scan rates 0.1, 0.05, 0.02 and 0.01 were studied for $1.67*10^{-5}$ N KMnO₄ in 0.1 M KCl at 16.7 °C as illustrated in Fig.(2)..The effect of scan rate on redox behavior of KMnO₄ ($1.67*10^{-5}$ N) was found to decrease with the decrease in scan rate value indicating diffusion reaction mechanism. The effect of scan rate data given in Table (2) prove the diffusion character of redox reaction which appeared from the increase in cyclic voltammetry data with decrease of V^{1/2}.

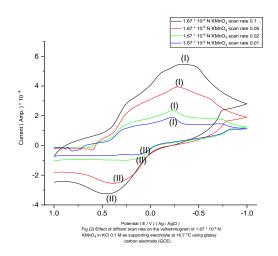


Table (2) : Cyclic voltammetry and kinetic parameters (D_a , D_c , k_s , Γ_c , Q_c , Γ_a and Q_a) for redox peak couples (I and II) of different scan rates of $1.67*10^{-5}$ N KMnO₄ in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode

						(G	CE).							
v^(1/2) V/Sec.	Ep _a (volt)	Ep _c (volt)	ΔEp (volt)	Ip _a /Ip _c	E° (volt)	Da x10 ⁶ cm ³ /sec.	Dc x10 ⁵ cm ³ /sec.	Ep _{c/2} (volt)	αn _a	$\begin{array}{c}k_{s} x\\10^{-3}\\\text{cm/sec.}\end{array}$	$\frac{\Gamma_{c}}{x10^{7}}$ mol/cm ²	$(+) Q_c x 10^4 colom$	$\Gamma_a \ x10^8 \ mol/cm^2$	$\begin{array}{c} \text{(-)} \ Q_a \\ x 10^4 \\ \text{Colom} \end{array}$
0.316	0.429	-0.318	0.747	0.692	0.0555	3.10	0.648	0.109	0.1090	11.4	0.267	1.62	1.85	1.12
0.223	0.063	-0.682	0.745	0.516	-0.3095	2.94	1.10	0.337	0.0455	6.56	0.494	2.99	2.55	1.54
0.141	0.048	-0.712	0.760	0.479	-0.3320	2.57	1.12	0.360	0.0433	5.50	0.787	4.77	3.77	2.28
0.100	-0.021	-0.745	0.724	0.435	-0.3830	3.80	2.00	0.382	0.0412	2.47	1.49	9.03	6.48	3.93

3.2. Oxidation reaction of succinic acid by KMnO₄

On adding different concentrations of succinic acid ranging from $5.26*10^{-6} - 2.17*10^{-5}$ M to $1.43*10^{-5}$ N KMnO₄ only one cathodic peak ranging from -0.1V - 0.25 V and one anodic peak ranging from 0.5 V - 0.8 V as showed in Fig.(3). The negative shift of the cathodic peak potentials indicates the oxidation of succinic acid by permanganate ion because of the decrease in reduction process. Also, the oxidation of succinic acid is achieved from the positive shift

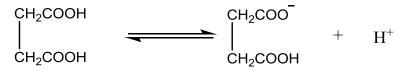
ak potentialscomplexes (1) and (2).anganate ionThe interaction suggested mechanism is illustrated as inAlso, thethe following equations:

in the potentials of the resulted anodic peaks. The different

shift in reduction peak potentials which is not regular can be

explained by the different complexes as a result of oxidation

of succinic acid with permanganate forming suggested



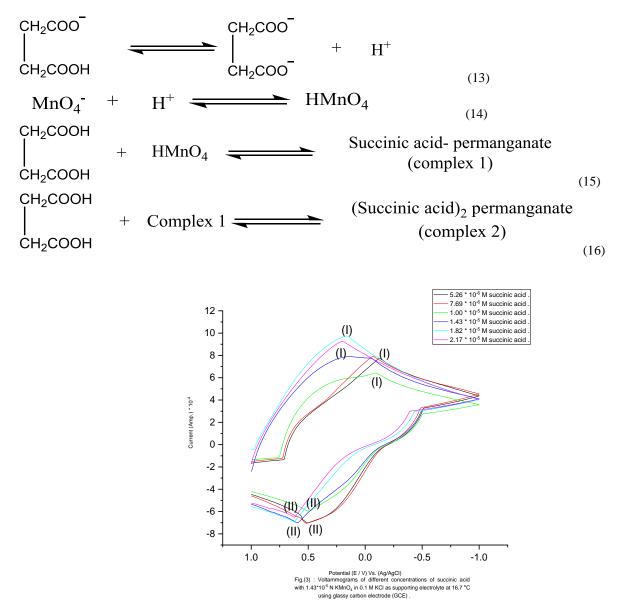


Table (3a): Cyclic voltammetric and kinetic parameters ($D_a, D_c, k_s, \Gamma_c, Q_c, \Gamma_a$ and Q_a) of reduction peak couples (I) and oxidation peak couples (II) for different concentrations of succinic acid with 1.43*10⁻⁵ N KMnO₄ in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode (GCE)

			suppor	ing elect	rolyte at .	10.7 C	using g	lassy ca			JCE).			
[M] x10 ⁵ mol.eqv/t	Ep _a (volt)	Ep _c (volt)	ΔEp (volt)	Ip _a /Ip _c	E° (volt)	Da x10 ⁵ cm ³ /S	$Dc \\ x10^5 \\ cm^3/S$	Ep _c / 2 (volt)	αn_{ac}	$\begin{array}{c} k_s \; x \\ 10^{-3} \\ \text{cm/sec.} \end{array}$	Γ_{c} x10 ⁸ mol/cm ²	$(+) Q_c x 10^4 C$	$\Gamma_a \ x10^8 \ mol/cm^2$	(-) Q _a x10 ⁴ C
1.58	0.497	-0.127	0.624	0.9835	0.185	4.57	4.73	0.385	0.0906	2.40	6.85	4.15	6.74	4.08
1.54	0.462	-0.069	0.531	0.9691	0.1965	4.46	4.75	0.366	0.1066	0.406	6.69	4.05	6.48	3.93
1.50	0.456	-0.048	0.504	1.0634	0.2040	3.73	3.30	0.594	0.0722	0.162	5.44	3.29	5.78	3.50
1.43	0.039	0.740	0.701	0.7735	0.3895	1.36	2.27	0.895	0.2992	14.1	4.29	2.60	3.32	2.01

1.36	0.026	0.749	0.723	0.6247	0.3875	0.647	1.77	0.871	0.3802	21.2	3.50	2.12	2.19	1.33
1.30	0.023	0.784	0.761	0.5929	0.4035	0.621	1.66	0.905	0.3833	46.9	3.46	2.09	2.05	1.24

The oxidation stability constant (β_{MX}) for interaction of KMnO₄ and succinic acid in 0.1 M KCl is calculated by applying equation (17) [25 – 32].

 $(E_{1/2})_{C}-(E_{1/2})_{M}=(2.303 \text{ RT/nF}) (\log \beta_{MX})+(2.303 \text{ RT/nF})(\log C_{X})$ (17)

Here $(E_{1/2})_M$ is the half wave potential for KMnO₄ in absence of succinic acid , $(E_{1/2})_C$ is the half wave potential in presence of succinic acid .

The oxidation Gibbs free energies for interaction between $KMnO_4$ and succinic acid can be calculated by the use of equation (18).

 $\Delta G = 2.303 \text{ RT} \log \beta_{MX}$

(18)

The calculating thermodynamic parameters β_{MX} and ΔG for the oxidation of succinic acid by permanganate are given in Table (3b). The positive ΔG values indicated that the complexation was taken place also after oxidation of succinic acid, complexes (1) and (2) may be formed. These values were increased by increasing of succinic acid concentrations.

Table (3b): Cyclic voltammetric data (log β_{MX} and ΔG) of reduction peak couples (I) and oxidation peak couples (II) for
different concentrations of succinic acid with 1.43*10 ⁻² N KMnO ₄ in 0.1 M KCl as supporting electrolyte at 16.7 °C using
glassy carbon electrode.

[M] x10 ² Mol.equiv./lit.	[L] x10 ² Mol.eqv./lit.	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	log[L]	$log \; \beta_{MX}$	ΔG (KJ/mol)
1.58	0.526	0.0555	0.1850	0.1295	-2.28	5.26	29.2052
1.54	0.769	0.0555	0.1965	0.1410	-2.11	5.96	33.0748
1.50	1.00	0.0555	0.2040	0.1485	-2.00	6.49	36.0559
1.43	1.43	0.0555	0.3895	0.3340	-1.85	13.46	74.6921
1.36	1.82	0.0555	0.3875	0.3320	-1.74	13.86	76.9444
1.30	2.17	0.0555	0.4035	0.3480	-1.66	14.87	82.5337

3.3. Effect of scan rates on the oxidation of succinic acid by KMnO₄

Fig (4), Tables (4a) and (4b) illustrate the effect of scan rates on the redox potential characterizing of $KMnO_4$ reaction with succinic acid which proves the diffusion

control reaction because of the decrease in analysis values by decrease of the scan rate.

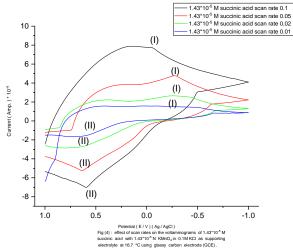


Table (4a) : Cyclic voltammetric and kinetic parameters (E_{Pa} , E_{Pc} , I_{Pa}/I_{Pc} , D_a , D_c , k_s , Γ_c , Q_c , Γ_a and Q_a) for redox peak couples (I, II) at different scan rates of 1.43×10^{-5} M succinic acid with 1.43×10^{-5} N KMnO₄ in 0.1 M KCl as supporting electrolyte and at 16.7 °C using glassy carbon electrode (GCE)

			supportir	ig electro	olyte and	<u>d at 16.7 °</u>	using gla	assy cal	rbon el	ectroae	<u> (GCE).</u>			-
v^(1/2) v/sec.	Ep _a (volt)	Ep _c (volt)	ΔEp (volt)	Ip _a /Ip _c	E° (volt)	Dax10 ⁵ cm ³ /sec.	Dcx10 ⁵ cm ³ /sec	Ep _{c/2} (volt)	αn _a	$\begin{array}{c} k_s \; x \\ 10^{-1} \\ \text{cm/sec.} \end{array}$	$\Gamma_c x 10^7$ mol/cm ²	(+) Q _c x10 ⁴ C	$\Gamma_a x 10^8$ mol/cm ²	(-) Q _a x10 ⁴ C
0.3162	0.039	0.740	0.701	0.7735	0.3895	2.27	2.27	0.895	0.299	1410	0.429	2.60	4.29	2.60
0.2236	0.035	-0.377	0.412	0.4177	-0.171	0.450	2.58	0.575	0.049	1.32	0.647	3.92	2.70	1.64
0.1414	0.033	-0.393	0.426	0.4703	-0.180	0.271	1.23	0.625	0.046	0.737	0.706	4.28	3.32	2.01
0.1000	0.029	-0.464	0.493	0.5279	-0.218	0.469	1.69	0.837	0.036	2.07	1.17	7.09	6.18	3.74

Table(4b): Cyclic voltammetric data ($\log \beta_{MX}$ and ΔG) for redox peak couples (I , II) at different scan rates on stability constant for reaction (1 : 1) of 1.43 *10⁻² N KMnO₄ with 1.43*10⁻² M succinic acid in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode (GCE).

υ (V/S)	[M] x10 ² mol.eqv./lit.	[L] x10 ² mol.eqv./lit.	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	log[L]	$log \; \beta_{MX}$	ΔG (KJ/mol)
0.1	1.43	1.43	0.0555	0.3895	0.3340	-1.85	13.46	74.6921
0.05	1.43	1.43	-0.3095	-0.1710	0.1385	-1.85	6.660	36.9663
0.02	1.43	1.43	-0.3320	-0.1800	0.1520	-1.85	7.130	39.5715
0.01	1.43	1.43	-0.3830	-0.2175	0.1655	-1.85	7.599	42.1765

Figs. (5) and (6) represent the relation between $I_P \& V^{1/2}$ in absence and presence of succinic acid:

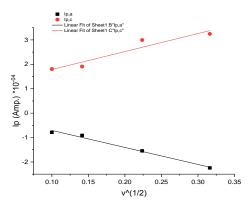


Fig. (5): Relation between I_P vs. V^{1/2} for redox peak couples (I, II) of 1.67*10⁻⁵ N KMnO₄ in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode (GCE) in absence of succinic acid.

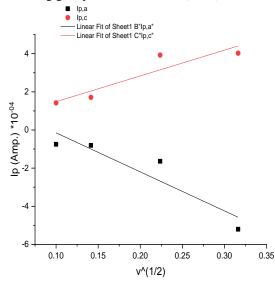


Fig (6): Relation between I_P vs. V^{1/2} for redox peak couples (I, II) reaction of 1.43*10⁻⁵ N KMnO₄ with 1.43*10⁻⁵ M succinic acid in 0.1 M KCl as supporting electrolyte at 16.7 °C using glassy carbon electrode (GCE).

Conclusion:

- Cyclic voltammograms of KMnO₄ was done and the redox peaks were explained.
- Oxidation of succinic acid by permanganate was illustrated and explained.
- The mechanism of redox reaction for the interaction between succinic acid and potassium permanganate was suggested.
- Formation of complex after oxidation was observed for the oxidation of succinic acid with KMnO₄.

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