Oxidation of oxalic acid by ammonium metavanadate in aqueous Kcl solutions Cyclic Voltammetrically

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Abstract: In the present work, the oxidation behavior of oxalic acid with NH_4VO_3 was examined via cyclic voltammetry in KCl aqueous solution. The cyclic voltammetry gave a reversible redox couple of waves for NH_4VO_3 in the absence and presence of oxalic acid due to the reduction effect of +5 vanadium ion to +4 one. Also, the oxidation effect was discussed by the oxidation peak in the reverse direction. The positive shift in the potential of both the oxidation and reduction peaks of NH_4VO_3 in the presence of oxalic acid supports the oxidation mechanism. The oxidation stability constants and Gibbs free energies of oxidation resulting from the interaction of NH_4VO_3 on oxalic acid were evaluated and their data were discussed.

keywords: Oxalic acid, oxidation, ammonium metavanadate, oxidation stability constant, Gibbs free energy of complexation.

1.Introduction

The electro chemical behavior of vanadate ion is studied in acidic and alkaline solutions. The redox behavior of V (V) / V (IV) couple was examined by some authors in acidic solutions by the use of different electrodes (1-4). The redox flow battery system used the V (V) / V (IV) redox couple reaction has been developed using aqueous electrolytes (5). Therefore the electrochemical and physical characters of NH_4VO_3 are needed. Cyclic voltammetry measurements were carried out in a 30 ml glass cell. Cyclic voltammetry was achieved with computer controlled Auto lab DY2000 (USA). All runs were done with three electrode systems Pt wire counter electrode, standard electrode (Ag/AgCl), small glassy carbon (SGCE) was applied as a working electrode. The SGCE was carefully polished by aluminum oxide emery paper and rinsed with deionized water.

2. Experimental:

The NH_4VO_3 is of the type BDH, whereas KCl and oxalic acid are from Sigma Aldrich Co. Bi distilled water with a conductance of 2.5 micro Siemens, μ ohm^{-1} was used. Cyclic voltammetry potentiostat of the type DY2000 was used for the measurements at different scan rates and after passing nitrogen gas for 10 minutes in each solution to remove the dissolved oxygen.

3.Results and discussion:

Cyclic voltammetry of NH_4VO_3 alone

Cyclic voltammetry for the redox behavior of NH_4VO_3 alone in 0.1 M Kcl was studied in range from -0.6 V to 1.25 V. The reduction proceeded at approximately 0.26 V where the oxidation happened by using one wave at 0.29 V. ΔEp are arranged from 0.01650 to 0.2665 for all the different NH_4VO_3 concentrations in 0.1 M Kcl at 16^0 C indicating the reversibility of the redox processes. The mechanism can be suggested as (1-4):

$VO_2^+ + 2 H^+ + e^- \leftrightarrow VO^{2+} + H_2O$ whereas the oxidation peak proceeds at $\approx$ 0.29 V through the opposite equation.

of the reduction mechanism

The electro chemical obeys Randles-Sevcik (4) equation which increases in current/ potential by increasing NH_4VO_3 concentration.

For our reversible redox couples the peak current is given by Randles-Sevcik equation (1): (6, 7, 8)

$$i_p = (2.69 \times 10^5)\, n^{1.5} A\, D^{0.5}\, \nu^{0.5}\, C \qquad \text{(Eq. 1)}$$
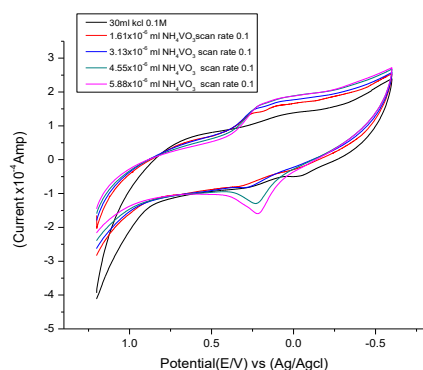
Diffusivity of NH_4VO_3 ions in KCl

Fig. (1) Displays the voltammograms of different NH_4VO_3 concentrations in 0.1 M KCl aqueous at scan rate 0.1.

Where A is the area of electrode (in cm^2), D is the diffusivity of the primary reactant in the electrolyte (in cm^2/sec),C is bulk concentration (in mole/cm^3), n is number of electrons and $\sqrt{}$ is the scan rate (v/sec). For irreversible redox couple, ip can be calculated by equation (2): (9)

$$i_p = (2.99 \times 10^5)\, n^{1.5} A\, D^{0.5}\, \nu^{0.5}\, C\, \alpha^{0.5} \quad \text{(Eq.2)}$$

Where α is the charge transfer coefficient and quantity of electricity consumed during the cathodic scan is calculated by the use of equation (3): (10-15)

$$Q_c = n\, F\, A\, \Gamma_c \qquad \text{(Eq.3)}$$

The heterogeneous rate constant for electron transfer is calculated by applying equation (4): (15-20)

$$k_s = 2.18*[D_C\ \alpha n_a\ F\ \nu/RT]^{1/2}\ *\exp\ [\alpha^2 nF\ \Delta E_p/RT] \qquad \text{(Eq.4)}$$
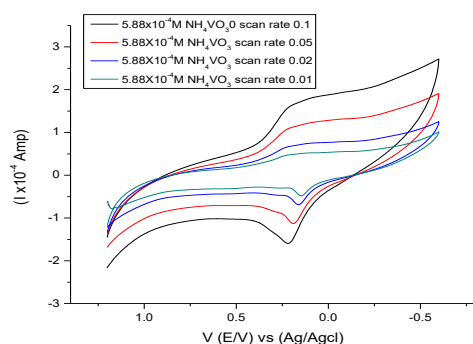

Fig2. Various scan rates (5.88×10^{-4} M of NH_4VO_3, 16^0 C)

As well as the relation between i_p vs υ confirms the diffusion control reaction as shown in Figure 3.

Where E_p and $E_{p/2}$ are the peak potential and its corresponding half wave potential.

The $\alpha\ n_a$ for reversible reaction can be calculated by applying equation (6): (7, 8)

$$(Epc - E_{pc}/2) = 1.857RT\,/\,\alpha\, n_a\, F \qquad \text{(Eq.6)}$$

$$E_p - E_{p/2} = 59.6\,/\,\alpha$$

$$0.13325\ \alpha = 59.6$$

$$\alpha = 0.447$$

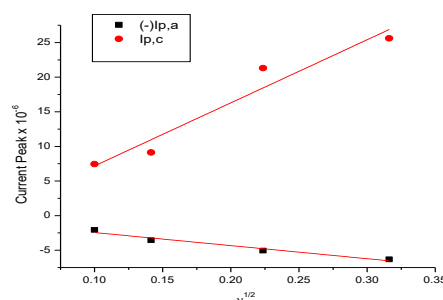$$\alpha\ n_a = 0.455$$

$$n_a \approx 1.01$$

Fig 3. Peak current and $\nu^{1/2}$ for NH_4VO_3.

Oxidation reaction (oxalic acid by NH_4VO_3)

On adding different concentrations of oxalic acid ranging from 2.86×10^{-6} M to1.05×10^{-5} M we observe no extra peaks other than the reduction and oxidation NH_4VO_3 peaks.The positive shift of both the reduction and oxidation NH_4VO_3 peaks by adding oxalic acid proves the oxidation process of oxalic acid can be calculated by the use of equation (5):(7,9)

$$E_{p} - E_{p/2} = 47.7mv\,/\,\alpha \qquad \text{(Eq.5)}$$

$$0.13325\ \alpha = 0.47$$

$$\alpha = 0.560$$

$$\alpha\ n_a = 1.354$$

$$n_a = 2.41 \approx 1.11$$

The calculated $\alpha\ n_a$ data according to the last equation are represented in Table (1) for the effect of different concentrations of NH_4VO_3, n_a is the number of electrons. On applying both equations 5 and 6 for evaluating the number of electrons we obtained an average 1.11e on (21) using equation 5 and $\approx$ 1.0178e on the use of equation 6 which indicates the applicability of equation for explaining our reversible redox reaction. The charge transfer coefficient calculated has a mean value of $\approx$ 0.447. Surface coverage which denotes the electrode surface

covered by electro active species is calculated by equation 7 (7-10) for the cathodic scan.

$$\Gamma_c = i_{p,c}\, 4RT/n^2 F^2 A\, \nu \quad (Eq.\ 7)$$

Where R is universal gas constant, F Faraday constant, A surface area of the working.

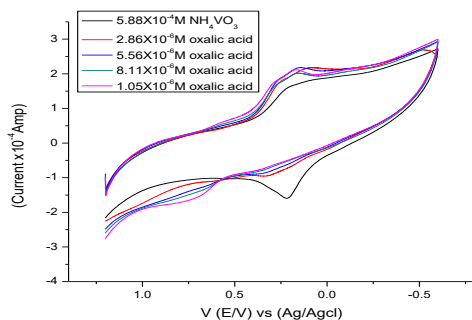electrode in cm^2, n the number of electrons, ν is the scan rate vs^{-1}

Fig 4. Various concentrations of oxalic acid (16^0 C , ν =0.1).

The oxidation stability constant (β_{MX}) for the interaction of NH_4VO_3 with oxalic acid in 0.1

M KCl is calculated by applying equation (8) (22,23,24)

$$\Delta E^\circ = E^\circ_C - E^\circ_M = 2.303(RT/n\ F)\ *(\log \beta_{MX} + j \log C_L) \quad (Eq.8)$$

Here $(E_{1/2})_M$ is the half wave potential of NH_4VO_3 in the absence of oxalic acid, $(E_{1/2})_C$ is the half wave potential 0f NH_4VO_3 in the presence of oxalic acid. The oxidation Gibbs free energies for the interaction between NH_4VO_3 and oxalic acid is calculated by the use of equation (9) (22,24)

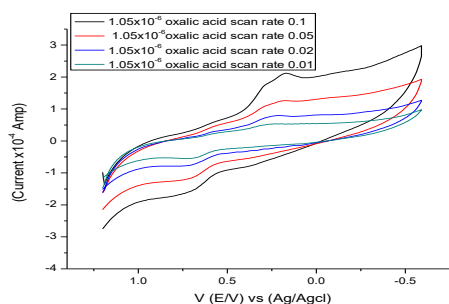$$\Delta G = -2.303\ RT \log \beta_{MX} \quad (Eq.9)$$

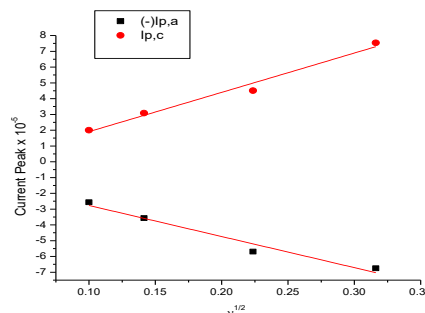**Fig5.** Various scan rates for complex (NH_4VO_3 /oxalic acid)

Fig 6. Peak current and $\nu^{1/2}$ of complex (NH_4VO_3 and oxalic acid).

Figures 5 and 6 illustrate the effect of scan rate on the redox potential characterization ofNH_4VO_3 and oxalic acid proves the diffusion controlled reactions according to the decrease in solvation parameters given in

Kcl aqueous solutions at 16^0c. Table 1. Various concentrations of NH_4VO_3 (16^0 C , ν =0.1) All parameters cited in

All the evaluated parameters for the cathodic peak and the same procedure for that of the anodic peak are given in Table (1) for the effect of different NH_4VO_3 concentrations in 0.1 M

Table (1) are increased with the increase of NH_4VO_3 concentrations

[M] x10^6 mol cm^-3	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	(-)Ip,a x10^5 (Amp.)	Ip,c x10^5 (Amp.)	Ip,a/Ip,c	E°(volt)	Dax10^6 cm^2/s	Dcx10^6 cm^2/s	αnac	Ks x10^2	Γ cx10^9 mol /cm^2	(+) Qc x10^5c	Γ ax10^9 mol/cm^2	(-)Q a x10^5c
1.610	0.2992	0.2665	0.0327	0.950	2.60	0.3650	0.2829	0.5910	4.440	1.3545	2.060	2.1406	1.30	0.7813	4.730
3.130	0.2822	0.2159	0.0664	1.380	4.560	0.3030	0.2490	0.3333	3.630	0.6204	2.490	3.7517	2.270	1.1369	0.6890
4.55	0.2218	0.1999	0.0218	5.080	6.10	0.8322	0.2108	2.1244	3.070	0.6264	0.9390	5.0162	3.040	4.1746	2.530
5.88	0.2078	0.1650	0.0428	6.750	7.540	0.8959	0.1864	2.250	2.80	0.4558	1.160	6.201	3.760	5.5552	3.370

Table 2. Various scan rates ($5.88x10^{-4}$ M of NH_4VO_3, 16^0C)indicating the diffusion controlled reactions.The effect of scan rate for $5.88x10^{-4}$ M NH_4VO_3 prove the diffusion control reaction also, as the solvation and kinetic parameters are decreased with the decrease in scan rate as shown in Fig.(2) and Table(2)

υ	Ep,a volt	Ep,c volt	ΔEp volt	(-) Ip,ax10^5 Amp	Ip,cx105A mp	Ip,a/Ipc	E°volt	Dax10^6 cm^2/s	Dcx10^6 cm^2/s	αna	Ks C x10^2	Γ c x10^8 mol /cm^2	(+) Qc x10^5 c	Γ a x10^8 mol /cm^2	(-) Q a x10^4 c
0.10	0.2078	0.1650	0.0428	6.750	7.540	0.8959	0.1864	2.250	2.80	0.4558	1.160	0.6201	3.760	0.5555	0.3370
0.05	0.1844	0.2287	-0.0443	5.690	5.690	1.2610	0.2066	3.190	2.0066	0.7636	0.1570	0.7425	4.50	0.9363	0.5670
0.02	0.1524	0.1968	-0.0445	3.570	3.570	1.1603	0.1746	3.140	2.3342	0.5207	0.0882	1.2662	7.67	1.4691	0.890
0.01	0.1349	0.2313	-0.0964	2.570	2.570	1.2842	0.1831	3.250	1.969	0.7055	0.0235	1.447	9.97	2.1122	1.280

Table 3. Various concentrations of oxalic acid (16^0 C)As shown in Figure 4 and Table 3, the obtained cyclic voltammetry data, E_{pa} , E_{pc} , ΔE_p , I_{pa} / I_{pc} , D_a , D_c , K_s , Q_c , Q_a , Γ a , Γ c are smaller than the same values in absence of oxalic acid indicating oxidation of oxalic acid by NH_4VO_3 in 0.1 M Kcl

[L]x10⁵ mol/cm³	[M] x10⁶ mol/cm³	Ep,a volt	Ep,c volt	ΔEp volt	(-) Ip,a x10⁶ Amp	Ip,c x10⁵ Amp	Ip,a/Ip,c	E° volt	Da x10⁸ Cm²/s	Dc x10⁶ Cm²/s	αnac	Ks x10²	Γc x10⁹ mol/cm²	(+) Qc x10⁵ c	Γa x10¹⁰ mol/cm²	(-) Qa x10⁶ c
0.2860	5.710	0.3222	0.2811	0.0412	9.940	6.320	0.1572	0.3016	5.1550	2.090	1.2893	1.640	5.2003	3.150	8.1750	4.950
0.5560	5.560	0.3040	0.3275	0.0235	8.020	5.250	0.1527	0.3157	3.550	1.520	1.6589	0.4330	4.3206	2.620	6.5956	4.00
0.8110	5.410	0.3352	0.3301	0.0051	6.640	3.750	0.1770	0.3326	2.5701	0.8210	1.7894	0.5860	3.0853	1.870	5.4603	3.310
1.050	5.260	0.3304	0.3545	-.0241	6.310	2.560	0.2464	0.3425	2.4503	0.4040	2.3091	0.260	2.1068	1.280	5.1912	3.150

The calculating thermodynamic parameters β_{MX} and ΔG for the oxidation of oxalic acid by NH_4VO_3 are given in Table 4.

Table 4. Stability constant for complex (NH_4VO_3 /oxalic acid)

[M]x10⁶mol / cm⁻³	[L]x10⁵mol / cm⁻³	(Ep,1/2)M	(Ep,1/2)C	ΔE mv	J(L/J)	Log βj	ΔG (KJ/mol)
5.710	0.2860	0.1864	0.3016	0.1152	0.5	6.7887	-37.5847
5.560	0.5560	0.1864	0.3157	0.1293	1	9.7634	-54.0540
5.410	0.8110	0.1864	0.3326	0.1462	1.5	12.7333	-70.4971
5.260	1.050	0.1864	0.3425	0.1561	2	15.3948	-85.2318

The very great ΔG negative values and also β_{MX} indicate the very strong interaction between oxalic acid and NH_4VO_3 which is oxidation reaction followed by complexation ones. The stability constant of (NH_4VO_3 /oxalic acid) as shown in Table 5 decrease by decreasing scan rates.

Table 5. Relation between stability constant and scan rate for complex (NH_4VO_3 /oxalic acid)

v	[M]x10⁶mol / cm⁻³	[L]x10⁵mol / cm⁻³	(Ep,1/2)M	(Ep,1/2)C	ΔE v	J (L/M)	Log βj	ΔG (KJ/mol)
0.1	5.260	1.050	0.1864	0.3425	-0.1561	1	-0.4616	2.5559
0.05	5.260	1.050	0.2066	0.3142	-0.1076	1	1.2267	-6.7912
0.02	5.260	1.050	0.1746	0.2320	-0.0574	1	2.9761	-16.4769
0.01	5.260	1.050	0.1831	0.1776	0.0055	1	5.1696	-28.6208

Table 6. Effect of scan rate on NH_4VO_3 and oxalic acid

v	Ep,a volt	Ep,c volt	ΔEp volt	(-Ip,ax)10⁶ Amp	Ip,c x10⁵ Amp	Ip,a/Ip,c	E° volt	Da x10⁸ cm²/s	Dc x10⁷ cm²/s	αna	Ks Cx10²	Γc x10⁹ mol/cm²	(+) Qc x10⁵c	Γa x10⁹ mol/cm²	(-) Qa x10⁵c
0.10	0.3304	0.3545	0.0241	6.310	2.560	0.2464	0.3425	2.4503	4.0358	2.3091	0.260	2.1068	1.280	0.5191	0.3150
0.05	0.3630	0.2654	0.0975	5.050	2.130	0.2370	0.3142	3.1367	5.5822	0.9818	1.620	3.5041	2.120	0.8306	0.5030
0.02	0.1994	0.2647	0.0653	3.550	0.913	0.3890	0.2320	3.8750	2.5610	1.7898	0.0375	3.7527	2.270	1.4597	0.8840
0.01	0.0740	0.2816	0.2080	2.060	0.744	0.2765	0.1776	2.5995	3.3996	1.2234	0.0014	6.1146	3.710	1.6909	1.020

Table 6 by the decrease of the scan rate

Conclusion:

Cyclic voltammetry of NH_4VO_3 was done and the redox peaks were explained. Oxidation of oxalic acid by NH_4VO_3 was illustrated and examined. Oxidation stability constant and Gibbs free energy of oxidation were evaluated and their data were explained. Also complexation is suggested for the interaction of NH_4VO_3 with oxalic acid after oxidation process.

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