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Cyclic voltammetry of redox reaction of lead acetate in presence of oxalic acid

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Abstract

Redox reaction for lead acetate in absence and presence of oxalic acid was studied by the use of cyclic voltammetry in 0.1M HNO_3 at 302.2K. The glassy carbon electrode (GCE) was used as working electrode, whereas Ag/AgCl was used as reference electrode and platinum wire was used as auxiliary electrode. The complexation stability constants and Gibbs free energies of complexation were evaluated.

Keywords: Lead acetate complexes, cyclic voltammetry, and stability constant, Gibbs free energy of complexation.
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1. Introduction

Cyclic voltammetry (CV) is a very useful method for explaining the interaction and stability interaction for some metal salts with organic chelating compounds [1-4]. (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species [5]. Ionic salts like copper, cadmium and lead salts can form complexes through the interaction with electron donating atom in the organic ligands like nitrogen, Sulphur, hydroxyl or carboxylic groups. The complex ability can be studied by the change in peak heights and shifts in both anodic and cathodic potentials as well as the half wave potential of measured peaks [6-8]. Lead (II) was chemically deposited on the chemically modified electrode (CME) by complexation with the modifier, and the electrode was transferred to an electrochemical cell for pulse voltammetric anodic stripping. The response depends on the concentration of lead in the bulk solution as well as the parameters involved in both the preconcentration and the measurement steps [9]. The aim of the present investigation is concerning the cyclic voltammetry studies of the redox reaction of lead acetate in absence and presence of oxalic acid in 0.1M HNO_3 at 302.2K. The complexation stability constants and Gibbs free energies of complexation were evaluated.

2. Experimental

Lead acetate, oxalic acid and nitric acid from Sigma Aldrich Company were used without purification. Bidestilled water with conductivity 2.5 micro ohm^{-1} was used.

A DY 2000 potentiostate was used for cyclic voltammograms developing at different scan rates. Pure N_2 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

The electrochemical behaviours for lead ions were studied voltammetrically in potential range from -2 V to +2 V vs Ag/AgCl electrode. Normally lead divalent ions showed one quasi reversible reaction (Fig.1). One oxidation peak was appeared at – 0.4 V in the forward and another reduction peak appeared at - 0.6 V at the reverse with 190 mV preparation peak potential (ΔE_P) is the difference between both anodic and cathodic peak potentials) similar to results obtained in literatures [10,11].

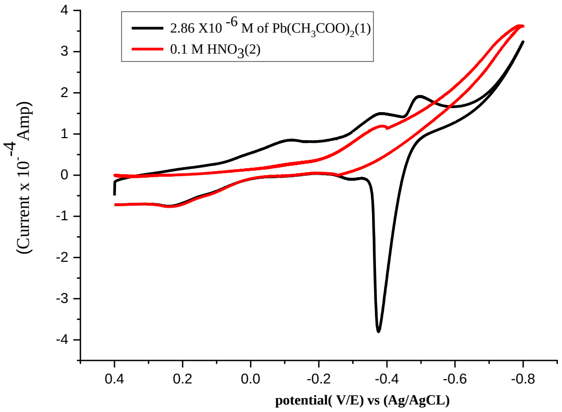

Fig (1): Cyclic voltamogram of 2.86 X 10 $^{-6}$M of $Pb(CH_3COO)_2$ and 0.1 M HNO_3 at 302.2 K , scan rate 0.1 v sec^{-1}

In studying the reduction scan, the one forward wave represents the reduction using two electrons whereas the oxidation scan in the reverse direction shows main oxidation peak consuming two electrons and the mechanism is:

$Pb^{+2} + 2\ e^- \longrightarrow Pb\ (s)$ for both reduction waves (1)
$Pb\ (s) \longrightarrow Pb^{+2} + 2e^-$ for main oxidation peak (2)

Analysis of the reduction and oxidation peaks:

The equations used for electrochemical voltammetric calculations for couple of peaks (1) and (2) are given in the following equations:

Firstly, the surface coverage which is the electrode surface area covered by the electroactive species is evaluated using the equation:

$$\Gamma = i_p\, 4RT / n^2 F^2 A\, \nu \qquad (3)$$

where R is gas constant, F is Faraday constant, A is surface area of the working electrode in cm^2, n is the number of electrons in redox reactions; ν is the scan rate in v s^{-1} and T is the absolute temperature.

Secondly the quantity of electricity consumed during the redox reactions which are evaluated by the equation (4) [12,13]:

$$Q = n\, F A\, \Gamma \qquad (4)$$

Diffusion coefficient was evaluated from Randles Sevick equation (5) [14-15]:

$$I_p = (2.69\text{x } 10^{-5})\; n^{3/2}\, A\, D^{1/2}\, \nu^{1/2}\, C \qquad (5)$$

where I_P is current in ampere. A is surface area of working electrode, D is diffusion coefficient in cm^3/sec, ν is the scan rate v $s^{-1}$and C is the concentration of lead acetate solution.

ΔE_P is the difference between both anodic and cathodic peak potentials represented in the following equation:

$$\Delta E_P = E_{Pa} - E_{Pc} \qquad (6)$$

The electron rate constant for transfer (k_s) from the working electrode surface and the reverse direction can be calculated by using the equation:

$$k_s = 2.18 * [D_C\, \alpha n_a\, F\, \nu / RT]^{1/2} * \exp\, [\alpha^2 nF\, \Delta E_P / RT] \qquad (7)$$

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

$$(E_{pc} - E_{pc/2}) = 1.857\, RT / \alpha n_a F \qquad (8)$$

Since $E_{pc/2}$ is the half wave potential for cathodic peak and α equal 0.5 as approximation for quasi reversible systems [16]. The above parameters are calculated for both anodic and cathodic waves used symbolled as (a) for anodic peak and (c) for cathodic peak.

The evaluated parameters , E_{Pa}(anodic wave potential), I_{Pc}(anodic peak current) , D_a anodic diffusion coefficient , k_s electron rate constant , Γ_a (anodic surface coverage , Q_a anodic quantity of electricity are increased with increase lead acetate concentration in 0.1 M HNO_3 (see Table (1) and Fig. (2)).

The same parameters were evaluated for the cathodic peak is increased by increase of lead acetate concentration favoring more diffusion-controlled reaction.

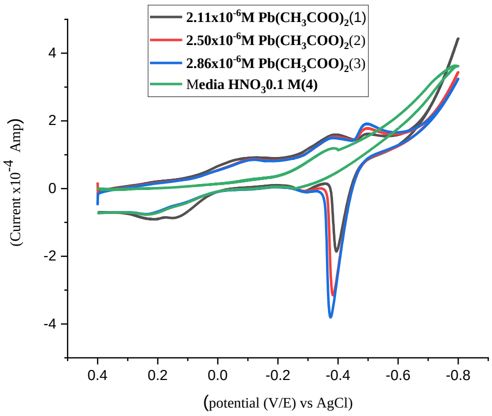

Fig (2): Cyclic voltamograms of different lead acetate concentrations in 0.1 M HNO_3 at 302.2 K, scan rate (0.1 v/sec)

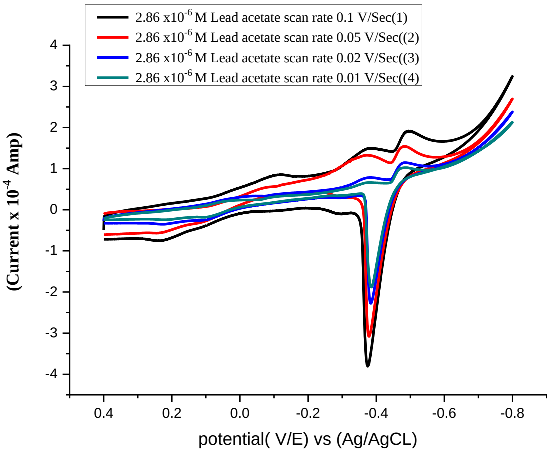

Fig (3): Effect of scan rate on 2.86 x10 $^{-6}$ M lead acetate in 0.1 M HNO_3 at 302.2 K

The effect of different scan rates 0.01, 0.02, 0.05 and 0.1 v s^{-1} were studied for 2.86 X10 $^{-6}$ M $Pb(CH_3COO)_2$ in 0.1 M HNO_3 at 302.2 K . It was found that the cyclic voltammetric data are decreased with decrease of the scan rates (See Table 2, Fig .3) favouring diffusion-controlled reaction. On adding different concentrations of oxalic acid ranging from $4.55\text{x}10^{-7}$ M to $2.22\text{x}10^{-6}$ M to $2.86\text{x}10^{-6}$ M of lead acetate solution, negative shifts in cathodic peaks and positive shift in anodic peak favouring more complexation. Also the peak integrities are increased in current favouring the decrease in ion-ion association for $Pb(CH_3COO)_2$ on adding oxalic acid as shown in Fig .(4) and Table (3).

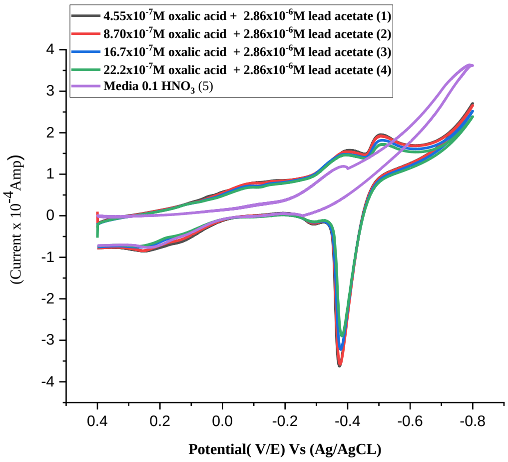

Fig. (4): Effect of different concentration of oxalic acid on cyclic voltamograms of 2.86 x 10^{-6} M lead acetate in 0.1 HNO_3 at 302.2 K (scan rate 0.1 v/sec)

As shown in Table (3), the obtained cyclic voltammetry data E_{Pa} , E_{PC}, ΔE_P , I_{Pa}/I_{Pc}, D_a ,D_c ,k_s , Γ_a ,Γ_c,Q_C and Q_a are smaller than the same values in absence of oxalic acid indicating the formation of complex between lead acetate and oxalic acid.

Effect of scan rates in complex formation

The kinetic and solvation parameters (k_s, Γ, Q and D) for the complex formation between lead acetate with oxalic acid at 302.2K for (0.1, 0.05, 0.02, 0.01 v/sec) scan rates are shown in (Fig.5). The effect of different scan rates of oxidation, anodic reduction potential and current for the first wave represented in Table (4). The stability constant (β_{MX}) for interaction of lead acetate with oxalic acid in 0.1 M HNO_3 at 302 .2 K is calculated by applying the equation:

$$(E_1/2)_C - (E_1/2)_M = 2.303(RT/nf) \log \beta_{MX} + 2.303(RT/nf) \log \beta_L \qquad (10)$$

Here $(E_1/2)_M$ is the half wave potential for lead acetate in absence of oxalic acid , $(E_1/2)_C$ is half wave potential in presence of oxalic acid .

The Gibbs free energies for complexation resulting from the interaction of lead acetate with oxalic acid can be calculated by the use of equation (11) [16-27].

$$\Delta G = - 2.303 RT \log \beta_{MX} \qquad (11)$$

The calculating thermodynamic parameters, β_{MX} and ΔG for complexation of lead acetate with oxalic acid are represented in Tables (5 and 6) indicating the complexation characters.

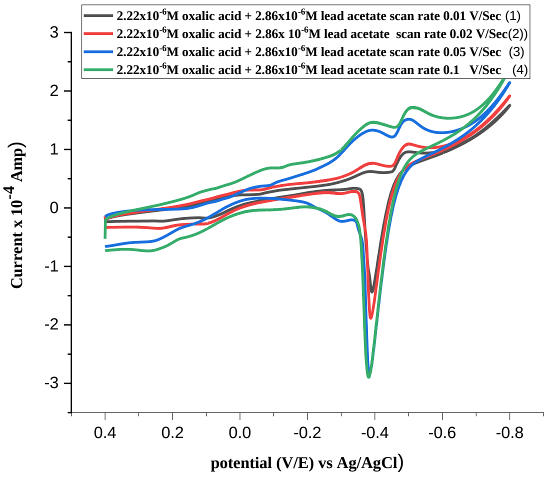

Fig (5): Effect of scan rate of 2.22 x 10^{-6} M oxalic acid on cyclic voltamograms of 2.86 x 10^{-6} M lead acetate in 0.1 HNO_3 at 302.2 K

Table (1): Solvation and Kinetic parameters (D, k_s, Γ and Q) of Lead acetate in the absence of (oxalic acid) at 302.3 K, in 0.1 M HNO_3 scan rate 0.1 V/Sec

$Mx10^6$ mol/cm^3	$Ep_{,a}$ volt	$Ep_{,c}$ volt	ΔEp (volt)	$ip_a x10^4$ (Amp)	$ip_c x10^5$ (Amp)	$ip_a/$ ip_c	Da mol/cm^2	Dc $x10^6$	$Ep_{c/2}$	αn_a	ks $x10^1$ cm/sec	Γ_c $x10^9$ (mol/cm^2)	(+) Q_c $x10^5$	Γ_a $x10^8$ (mol/cm^2)	(-) Q_a $x10^4$
2.11	-0.39	-0.49	0.1	2.13	2.86	7.466	0.0001	3.22	-0.46	1.6126	0.664	2.4559	1.49	1.833	1.11
2.50	-0.37	-0.49	0.12	3.57	4.78	7.468	0.0003	6.42	-0.47	4.8380	1.68	4.1143	2.49	3.072	1.86
2.86	-0.37	-0.49	0.12	3.85	5.72	6.733	0.0003	7.03	-0.47	2.4190	1.76	4.9199	2.98	3.312	2.01

Table (2): Solvation and Kinetic parameters (D, k_s, Γ and Q) of effect of scan on final addition of lead acetate2.86 x 10^{-6} M in the absence of (Oxalic Acid) in 0.1 HNO_3 0.1 M at 302.3K.

Scan rateV/sec	$Ep_{,a}$ (volt)	$Ep_{,c}$ (Volt)	ΔEp (Volt)	ip_a $x10^4$ (Amp)	ip_c $x10^5$ (Amp)	$ip_a/$ ip_c	Da $x10^4$	Dc $x10^5$	$Ep_{c/2}$	αn_a	Ks $x10^2$ cm/sec	Γ_c $x10^{-9}$ (mol/cm^2)	(+) Q_c $x10^8$	Γ_a $x10^8$ (mol/cm^2)	(-) Q_a $x10^4$
0.1	-0.38	-0.48	0.1	3.85	5.33	7.221	-0.43	3.19	-0.46	2.419	11.2	4.587	0.0978	3.312	2.01
0.05	-0.382	-0.477	0.095	3.26	4.93	6.597	-0.4295	4.55	-0.45	1.791	8.09	8.486	0.0885	5.598	3.39
0.02	-0.384	-0.48	0.096	2.60	4.14	6.274	-0.432	7.25	-0.45	1.612	6.57	17.81	0.0835	11.17	6.77
0.01	-0.387	-0.47	0.083	2.18	3.61	6.029	-0.4285	10.2	-0.44	1.612	4.47	31.08	0.0807	18.74	11.4

Table (3): Solvation and kinetic parameters of lead acetate in presence of oxalic acid in HNO_3 0.1 M at 302.2.15 K at scan rate 0.1 v/sec

$Mx10^6$ Lead acetate	Lx 10^7 Oxalic acid	$Ep_{,a}$ (Volt)	$Ep_{,c}$ (Volt)	ΔEp (Volt)	ip_a $x10^4$ (Amp)	ip_c $x10^5$ (Amp)	$ip_a/$ ip_c	Da	Dc $x10^6$	$Ep_{c/2}$	αn_a	ks $x10^1$	Γ_c $x10^9$ (mol/cm^2)	(+)Q_c $x10^5$	Γ_a $x10^8$ (mol/cm^2)	(-)Q_a $x10^{-5}$
2.86	4.55	-0.37	-0.5	0.13	3.76	5.26	7.068	0.00029	5.94	-0.47	1.612	1.60	4.522	2.74	3.196	1.96
2.86	8.70	-0.38	-0.51	0.13	3.72	4.99	7.542	0.00030	5.34	-0.48	1.612	1.52	4.287	2.60	3.234	1.94
2.86	16.0	-0.38	-0.51	0.13	3.29	4.85	6.782	0.00023	5.05	-0.47	1.209	1.28	4.170	2.53	2.828	1.71
2.86	22.2	-0.38	-0.5	0.12	3.04	4.11	7.389	0.00019	3.62	-0.48	2.419	1.27	3.533	2.14	2.611	1.58

Table (4): Effect of scan rate on the solvation and kinetic parameters (D, k_s, Γ and Q) on the addition of oxalic acid $2.22x10^{-6}$M with $2.86x10^{-6}$M lead acetate by molar ratio 1:1 in 0.1 M HNO_3 at 302.2 K.

Scanrate	$Ep_{,a}$	$Ep_{,c}$	ΔEp	ip_a	ip_c	$ip_a/$ ip_c	Da	Dc	$Ep_{c/2}$	αn_a	$ksx10^2$	Γ_c $x10^8$	(+) Q_c	Γ_a $x10^8$	(-) Q_a

V/sec	(volt)	(volt)	(volt)	x10^4 (Amp)	x10^5 (Amp)		mol/cm2	x10^5			cm/sec	(mol/cm^2)	x10^5	(mol/cm^2)	x10^4
0.1	-0.38	-0.51	0.13	3.04	4.11	7.3893	0.0002	0.3977	0.177	0.0704	2.74	0.3533	2.14	2.6111	1.58
0.05	-0.384	-0.49	0.106	2.87	3.72	7.7190	0.0003	0.6507	0.1	0.0834	1.70	0.6392	3.8	4.9340	2.99
0.02	-0.38	-0.49	0.11	2.24	3.39	6.6090	0.0005	1.3561	0.15	0.0755	1.60	1.4590	8.84	9.6429	5.84
0.01	-0.39	-0.48	0.09	1.74	2.79	6.2530	0.0007	1.8309	0.23	0.0681	0.849	2.3974	14.5	14.991	9.08

Table (5): Cyclic voltammetric data of lead acetate - oxalic acid in molar ratio (1:1) complexes in 0.1 HNO_3 M at 302.2 K (scan rate 0.1 v/sec)

Mx10^6 lead acetate	Lx10^7 oxalic acid	j	(E˚)M (Volt)	(E˚) C (Volt)	ΔE (Volt)	Log[L]	ΔG (KJ/mol)	log β_{MX}
2.73	4.55	0.166	-0.43	-0.44	0.01	-6.342	-8.0168	1.392
2.61	8.70	0.333	-0.43	-0.44	0.01	-6.060	-13.625	2.353
2.40	16.0	0.666	-0.43	-0.4445	0.0145	-5.795	-25.166	4.347
2.22	22.2	1	-0.43	-0.445	0.015	-5.653	-35.621	6.153

Table (6): Cyclic voltammetric data of lead acetate - oxalic acid complexes in 0.1 M HNO_3 at 302.2 K and different scan rate

υ	[lead acetate] x10^6	[oxalic acid] x10^6	(E˚)M (Volt)	(E˚) C (Volt)	ΔE (volt)	log[L]	ΔG (KJ/mol)	log β_{MX}
0.1	2.22	2.22	-0.43	-0.445	-0.015	-5.653	-29.832	5.153
0.01	2.22	2.22	-0.4295	-0.437	-0.0075	-5.653	-31.279	5.403
0.02	2.22	2.22	-0.432	-0.435	-0.003	-5.653	-32.148	5.553
0.05	2.22	2.22	-0.4285	-0.425	0.0035	-5.653	-33.402	5.769

3. Conclusion

Cyclic voltammetry of the redox reaction of lead acetate in absence and presence of oxalic acid in 0.1M HNO_3 at 302.2K was studied. The complexation stability constants and Gibbs free energies of complexation were evaluated. The increase current intensities of resulting peaks and the negative Gibbs free energy values obtained for the complexes indicate the complex characters between lead acetate and oxalic acid.

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