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Electrochemical study for redox reaction Thallous chloride in absence and presence of pectin in 0.1 M KF at 300.15K using glassy carbon electrode by cyclic voltammetry

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Abstract: The redox behavior data for thallous chloride in the absence and presence of pectin (1% w/w) using 0.1 M KF solution has been electro-chemically investigated using a cyclic voltammetry technique .were evaluated cyclic voltammetrically. This work emphasizes the current and potential sites at which monovalent thallous is reduced and oxidized in KF solutions that are vital to the electrochemical evaluation of thallium. The measurements were done for possible reduction and oxidation reactions by cyclic voltammetry experiment using a glassy carbon، silver-silver chloride، a platinum wire as working، reference, and a counter electrode. The effect of TlCl concentration for alone cyclic voltammetry and effect of pectin (1% w/w in H_2o) concentration were studied and their values were discussed. The difference in kinetic، thermodynamic parameters for interaction of TlCl with pectin (1% w/w) were evaluated and their values prove electrodes interaction between the two **.**

keywords: Redox reaction، Cyclic voltammetry، Thallous chloride، Pectin، Potassium fluoride

1.Introduction

Studying Thallium ions in solutions to evaluate their concentration because of the toxicity of it in the environment. Thallium was found to be less toxic than Cadmium and Mercury. Thallium is as toxic as lead and more toxic than Copper، Nickel and Zinc indicate caution needed [1] . Tl^+ has the same ionic radius as K^+ which can compete with K^+ at biological membranes and substitute it in metabolic processes [2] . We must summarize the knowledge gap about Thallium Furthermore، there is very little information available on Tl speciation in water and sediments collected in the field. Tl is small in scale include its use in rate poisons، clinical epilators, and some alloys. Tl is present in coal and such can enter the environment during coal mining and use in coal-lived power plants and other coal-based industrial processes. Tl is present in sulfide-rich ores mined for copper ، gold، lead، uranium, and zinc [3].

1. Experimental

Glassware، analytical balance، distilled water were used for the preparation of the solutions . Thallous chloride and potassium fluoride of the type BDH were used. Pectin from potassium chloride was also used as the other chemicals without purification to avoid their changes. The redox reaction was electrochemically measured using potentiostat of the type DY 2000 by subjecting the thallous chloride solution to cyclic voltammetry experiment، in which the cathodic and anodic current peaks were determined relative to used potentials. Cleaning of electrodes was done before the experiment، for revealing the surface of the electrodes which was covered with impurities. Nitrogen gas was passed through the measured solutions to avoid the presence of oxygen in the measured solutions.

Cyclic voltammetry Measurements

The cyclic voltammogram experiment was done with DY2000 potentiostat. The schematic of the setup is as shown in Fig.1.The applied potential was set between 0.75 to -1.25 V. The scan rate was set as 100 mv/s، and one is the number of cycles. During the measurement، the scanning potential was from 0.75 to -1.25 V ، and then back to 0.75 for a cycle. The measurement. This procedure was performed for all measurements and the peaks were recorded via the plot of current density as a function of potential [4].

Results and Discussion

The reduction and the oxidation peaks could be observed from the different voltammograms . The figures represent the current generated by the applied field for different TLCL concentrations in 0.1M KF at 300.15 K degree.

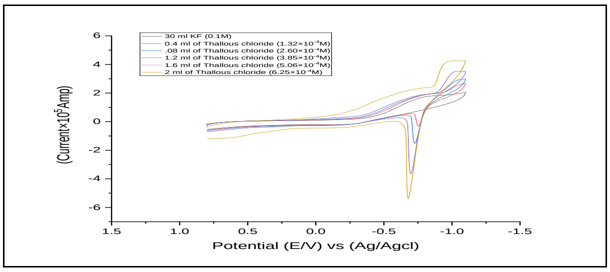

Fig.1. Effect of different concentrations of Thallous chloride in 0.1M KF using the glassy carbon electrode at 300.15K and scan rate 0.1V.S-1

In Fig.(1) reduction peak was reached at about -1V(Ep_c) and current density ~3×10 $^{-5}$ H (Ip_c) was generated. On the other hand, the complete oxidation of Tlcl was achieved at a potential Ep_a ~ -0.75 and current approximately ~3.2×10 $^{-5}$ A (Ampere) .

In absence of natural polymer pectin thallous ions shows some analysis parameters explained by different equations given in references [4-24]

We noticed that

1. the anodic peak potentials Ep_a are shifted to less negative potentials by increasing thallous ion concentrations.
2. the cathodic peak potentials are almost the same by increasing thallous ion concentration.
3. Anodic peak currents Ip_a and cathodic peak currents are largely increased by the increase in Tl^+ concentration.
4. The ratios between anodic peak currents and cathodic peak currents are great and increase with the increase in Tl^+ concentration indicating the anodic reaction is preferred to the cathodic reaction.

All the cyclic voltammetry analysis data are given in Table (1)

other than the electron transfer rate constant (Ks) of Tl^+ concentration indicating reversible and diffusion controlled redox reaction[30-35].

The difference in peak potentials ΔEp is big indicating the reaction is shifted towards quasirevesible processes [12].

Effect of scan rate on 6.25×10^{-4} M Tlcl in 0.1 M KF at 300.15 K was studied using glassy carbon electrode at scans 0.01 ، 0.02 ، 0.1 ، 0.05 V/S .

Most of the analysis parameters shown in Fig.(2), Fig (3) and Table (2) are increased by decrease of scan rate supporting the diffusion mechanism .

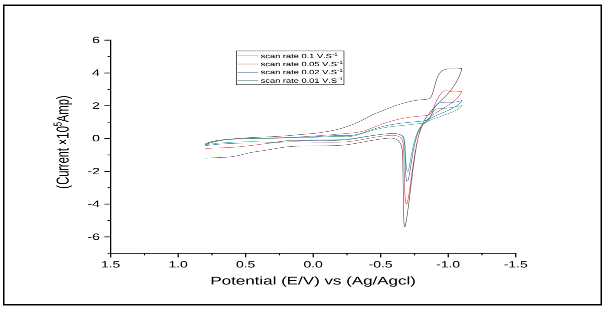

Fig.2. Effect of different scan rates of (6.25 x10^{-4} M) of Thallous chloride in 0.1M KF at 300.15K by the glassy carbon electrode

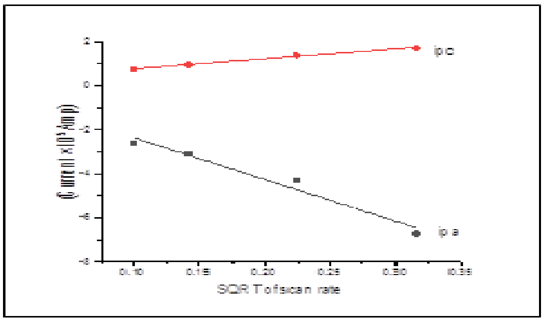

Fig.3. The relation between peak current and SQRT of scan rate for Thallous chloride alone

The given data in Table (2) show the following1.The relation between current density and √υ (square root) of scan rate (Fig.3) are straight lines.

2. The slope of the anodic peak is approximately equal 0.5 indicating the oxidation peak is more diffusion in character than the reduction peak.

3.The slope of the reduction peak is little than the oxidation wave on the reduction side.

Table (1): Effect of different concentrations of Thallous Chloride in 0.01M KF at 300.15K by the glassy carbon electrode.

[M] x10^4 mol.L^{-1}	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Da x10^9 $cm^2.s^{-1}$	Dc x10^{10} $cm^2.s^{-1}$	αnac	ksc x10^4 $cm.sec^{-1}$	Γ c x10^9 $mol.cm^{-2}$	(+) Qc x10^5 C	Γ a 10^8 $mol.cm^{-2}$	(-) Qa x10^5 C
1.32	-.753	-1.04	0.287	1.14	0.454	2.502	-.896	1.043	1.67	1.171	9.60	1.549	0.469	0.387	1.17
2.60	-.727	-1.04	0.313	2.19	0.774	2.826	-.883	0.994	1.24	0.800	8.82	2.643	0.801	0.747	2.26
3.85	-.710	-1.03	0.320	3.47	1.05	3.292	0.870	1.139	1.05	0.787	8.60	3.596	1.09	1.184	3.59
5.06	-.698	-1.02	0.322	4.01	1.37	2.939	-.859	0.880	1.02	0.738	8.36	4.662	1.41	1.370	4.15
6.25	-.669	-.938	0.269	6.72	1.72	3.897	0.803	1.619	1.07	1.021	6.02	5.885	1.78	2.293	6.95

Table (2): Effect of different scan rates of (6.25 x10^{-4} M) of Thallous chloride in 0.1M KF at 300.15K by the glassy carbon electrode

ν V.S^{-1}	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Dax10^9 $cm^2.s^{-1}$	Dcx10^{10} $cm^2.s^{-1}$	α nac	ksc x10^3 $cm.sec^{-1}$	Γ cx10^8 $mol.cm^{-2}$	(+)Qcx0^5C	Γ ax10^8 $mol.cm^{-2}$	(-) Qa x10^4 C
0.1	-669	-.938	0.434	6.72	1.72	3.897	.803	1.62	1.066	1.021	2.97	0.588	1.78	2.293	0.695
0.05	-688	.972	0.434	4.28	1.41	3.037	-.830	1.32	1.425	0.727	2.051	0.962	2.92	2.924	0.886
0.02	.694	-.933	0.338	3.07	0.975	3.150	-.813	1.69	1.703	1.091	0.686	1.663	5.04	5.241	1.591
0.01	-699	918	0.257	6.20	0.756	3.440	-.808	2.43	2.049	1.143	0.249	2.580	7.82	8.879	2.69

Table (3): Effect of different concentrations of pectin on Thallous chloride in 0.1M KF at 300.15K by the glassy carbon electrode

[M] x10^4mol.L^{-1}	[L] x10^4 mol.L^{-}	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-) Ip,a x10^5 Amp	Ip,c x10^5 Amp	Ip,a/Ip,c	E° Volt	Da x10^{10} $cm^2.s^{-1}$	Dcx10^0 $cm^2.s^{-1}$	αnac	kscx10^4cm. sec^{-1}	Γ c x10^9 $mol.cm^{-2}$	(+) Qc x10^5 C	Γ a x10^8 $mol.cm^{-2}$	(-) Qa x10^5 C
6.17	1.23	-.684	-.972	0.288	5.24	1.71	3.070	-.828	10.09	1.07	1.044	7.34	5.827	1.77	1.789	5.42
6.10	2.44	-.685	-.979	0.294	5.11	1.70	3.008	-.832	9.825	1.09	0.906	7.29	5.795	1.76	1.743	5.28
6.02	3.61	-.687	0.980	0.293	4.64	1.69	2.748	-.833	8.308	1.10	0.889	7.20	5.762	1.75	1.583	4.80
5.95	4.76	-.688	-.984	0.296	4.61	1.67	2.759	-.836	8.409	1.10	0.842	7.23	5.704	1.73	1.574	4.77
5.88	5.88	-.691	-.994	0.303	4.19	1.66	2.520	-.842	7.102	1.12	0.774	7.46	5.673	1.72	1.429	4.33

Table (4): stability constant for (Thallous chloride -pectin) complex

[M] x10^{-4} mol..L^{-1}	[L] x 10^{-4} mol.L^{-1}	(Ep,1/2)M	(Ep,1/)C	ΔE v	J (L/J)	Log βj	ΔG (KJ/mol)
6.17	1.23	-0.803	-0.828	0.0245	0.2	1.193	-6.856
6.10	2.44	-0.803	-0.832	0.0285	0.4	1.923	-11.054
6.02	3.61	-0.803	-0.833	0.03	0.6	2.568	-14.763
5.95	4.76	-0.803	-0.836	0.325	0.8	3.203	-18.410
5.88	5.88	-0.803	-0.842	0.039	1	3.885	-22.328

Effect of different concentrations of pectin on thallous chloride in 0.1 M KF .

Different natural polymer pectin (1% w/w in H_2O) concentrations the range of 1.23×10^{-4} to 5.88×10^{-4} was studied on Tl^+ ions in 0.1M KF at 300.15 K using glassy carbon electrode and the data are shown in Fig (4) and the resulted analysis data are given in Table (3)

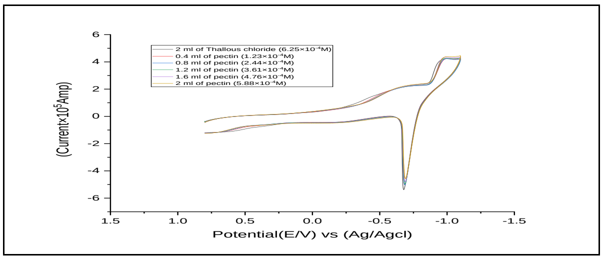

Fig.4. Effect of different concentrations of pectin on Thallous chloride in 0.1M KF at 300.15K by the glassy carbon electrod

From data given in table (3) show the following

1. The anodic diffusion coefficient D_a is decreased by more adding natural polymer pectin to thallous chloride in 0.1 M KF indicating the complexation reaction happened for TlCl + Pectin in the used electrolytic solution.

2. D_c is slightly affected by Pectin concentration indicating its little effect. Anodic surface coverage Γa ، cathodic surface coverage

3. Γc، the anodic quantity of electricity Q_a and cathodic quantity

of electricity, Q_c is decreased by more adding Pectin to the thallous solutions indicating complexation between TlCl and Pectin.

4. J value which is the stoichiometric ratio proves that the relation between metal and ligand M/L is small at a low concentration of natural polymer Pectin and increases with an increase in Pectin concentration till 1 . This means that the maximum stoichiometry at the used concentration is 1 :1.

In table (4) The stability constant evaluated for TlCl +Pectin Are somewhat small indicating electrostatic interaction between the two[26,35] . The Gibbs free energy of complexation has small values at small J values and increase till J=1 at molar ratio 1, metal [M] to ligand [L] , M/L [18,25] . The values of β and G at J =1 are also in range of strong electrostatic interaction [29,36] .

Conclusion

Voltammetry analysis data are increased by the increase in TlCl concentration indicating reversible and diffusion-controlled reaction.

The stability constants and Gibbs free energies of complexation for the interaction of TlCl with Pectin is increased by the increase in J values indicating strong electrostatic interaction

Declaration of Interests

The authors declare that they have no conflict with anybody about this work

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