



CYCLIC VOLTAMMETRIC STUDY OF Pb (II) IN DIFFERENT SODIUM SALTS AS SUPPORTING ELECTROLYTES

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ABSTRACT

The reduction of Pb (II) has been investigated in presence of different *sodium salts* as supporting electrolytes at a Hanging Mercury Drop Electrode (HMDE) using cyclic voltammetry. The correlation of cathodic peak current and anodic peak current, and the difference in cathodic peak potentials and anodic peak potentials with varying voltage scan rates indicates that the reduction of Pb (II) is reversible.

Key words: Cyclic voltammetry, Lead (II)

INTRODUCTION

On the basis of theory of stationary electrode voltammetry proposed by Nicholson and Shain¹, it was possible to develop diagnostic criteria by correlating kinetic and experimental parameters so that unknown systems can be characterized by studying the variations of peak current, half-peak potentials, or ratio of anodic peak currents and cathodic peak currents as a function of rate of voltage scan.

For a reversible system, the separation of anodic peak potential and cathodic peak potentials of the couple² is $57/n$ mV and the formal electrode potential is the average of the two peak potentials to a good approximation. If electron transfer reaction is irreversible system³, then peak to peak distance is large whereas in reversible system, the peak to peak distance is short.

The effect of a chemical reaction on the voltammetric wave will depend on its rate, as compared with the time required to perform the experiment. Taking reversible succeeding

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chemical reaction as an example, if a very rapid reaction is studied at very slow scan rates, the stationary electrode voltammogram will reflect the characteristics of the chemical step almost entirely.

On the other hand, if the rate of voltage scan is rapid as compared to the rate of reaction, the curves are identical to those for the corresponding uncomplicated charge transfer reactions. Hence in every kinetic case, the ratio of the rate constant to the rate of voltage scan appears in the kinetic parameter. This in turn, makes it possible to use these relations to define diagnostic criteria for investigation of unknown systems.

The relationship between scan rate (V) and I_{pa}/I_{pc} or I_{pc} vs $V^{1/2}$ is often used as diagnostic criteria for identifying the nature of the electrode process. Here, I_{pa} and I_{pc} are anodic peak current and cathodic peak currents in a cyclic voltammograms.

The authors have used these criteria to investigate the reduction of Pb (II) in different sodium salts as supporting electrolytes.

EXPERIMENTAL

Cyclic Voltammograph CV-27 (190 serial, Bioanalytical System Inc., U.S.A), in combination with an X-Y recorder (Bausch and Lomb Houston Instrument) was used to record the cyclic voltammograms.

A special cell having three-electrode assembly was used in which one of the electrode was hanging mercury drop electrode (HMDE)⁴⁻⁷, which was used as the working electrode and the platinum spiral was used as the auxiliary electrode. All the potentials were measured against Ag-AgCl electrode, which served as reference electrode. Nitrogen gas was used for deaeration and maintaining inert atmosphere over the test solution. All the experiments were carried out at $25 \pm 0.1^\circ\text{C}$.

Reagent grade chemicals and triple distill water was used for all experiments. The concentration of Pb (II) ion was kept at 1.0×10^{-3} M, while supporting electrolytes used were sodium chloride (NaCl), sodium hydroxide (NaOH) and sodium Sulphate (Na_2SO_4).

Cyclic voltammograms were taken at different scan rates varying from 40 mV/sec to 100 mV/sec. The starting and returning potentials were -0.0 volts and -1.0 volts, respectively.

RESULTS AND DISCUSSION

The cathodic peak potential and anodic peak potentials (E_{pc} and E_{pa}) and the peak potential difference (ΔE_p) were calculated from the cyclic voltammograms obtained in different sodium salts as supporting electrolytes (Table 1).

Table 1: Potential values of Pb (II) in different sodium salts as supporting electrolytes (in mV vs Ag-AgCl electrode)

S. No	Scan rates (mV/sec)	1 M NaCl			1 M NaOH			1 M Na ₂ SO ₄		
		E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p
1.	40	-0.46	-0.40	60	-0.41	-0.34	70	-0.40	-0.33	70
2.	50	-0.455	-0.40	55	-0.41	-0.36	60	-0.41	-0.33	80
3.	60	-0.45	-0.40	50	-0.41	-0.33	70	-0.42	-0.33	90
4.	70	-0.45	-0.40	50	-0.41	-0.35	60	-0.42	-0.33	90
5.	80	-0.44	-0.40	40	-0.41	-0.32	90	-0.42	-0.33	90
6.	90	-0.45	-0.40	55	-0.41	-0.34	70	-0.42	-0.33	90
7.	100	-0.45	-0.40	55	-0.41	-0.32	80	-0.43	-0.33	90

One of the criteria for reversibility is that $\Delta E_p = 57/n$ mV. It is clear from Table 1 that the value of peak potential difference for NaCl, NaOH, and Na₂SO₄, ΔE_p is higher than those expected for two electron change reaction and remains fairly stable at higher scan rates. The value of formal potential E_f calculated as the average of cathodic and anodic peak potentials agree fairly with the reported half-wave potential values of lead (-0.40 V vs SCE) in NaCl whereas they are little less in NaOH and Na₂SO₄.

It is further noted that ΔE_p remains fairly constant at lower scan rates, but increases slightly at higher scan rates. Hence reduction of Pb (II) is reversible in NaCl, NaOH and Na₂SO₄. However, the value of E_{pc} and E_{pa} are more negative in NaCl and Na₂SO₄ as supporting electrolyte than in NaOH.

The cathodic peak current (I_{pc}) and anodic peak current (I_{pa}) were measured at different scan rates for various sodium salts as supporting electrolytes. Results are given in Table 2, in which the values of I_{pa}/I_{pc} are also recorded.

Table 2: Value of cathodic and anodic peak currents in microamperes

S. No	Scan rates (mV/sec)	1 M NaCl			1 M NaOH			1 M Na ₂ SO ₄		
		I _{pc}	I _{pa}	I _{pa} /I _{pc}	I _{pc}	I _{pa}	I _{pa} /I _{pc}	I _{pc}	I _{pa}	I _{pa} /I _{pc}
1.	40	3.2	8.2	2.56	1.6	2.5	1.5	1.2	0.90	0.75
2.	50	3.5	8.3	2.37	1.7	2.6	1.5	1.2	1.2	0.96
3.	60	3.9	8.5	2.17	1.8	2.7	1.5	1.5	1.3	0.86
4.	70	4.2	8.7	2.07	2.0	2.9	1.4	1.6	1.2	0.75
5.	80	5.1	9.1	1.78	2.1	3.0	1.4	1.7	1.2	0.70
6.	90	5.7	9.7	1.70	2.4	3.4	1.4	1.9	1.4	0.73
7.	100	6.1	9.8	1.60	2.6	3.7	1.4	2.0	1.5	0.75

It is seen that the ration of I_{pa}/I_{pc} is not unity in any case. On increasing the scan rate, the ratio decreases regularly due to the fact that the cathodic peak current is enhanced at high scan rates. The plot of I_{pa}/I_{pc} vs scan rate in mV/sec is shown in Fig. 1.

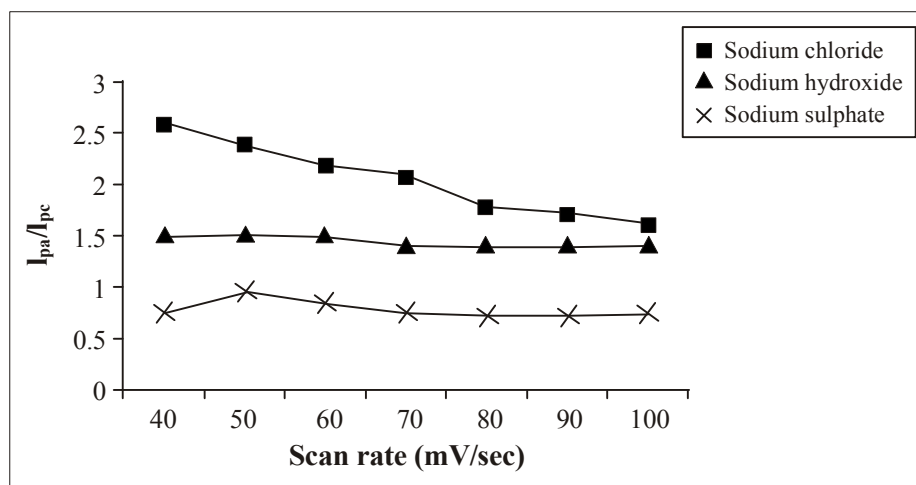


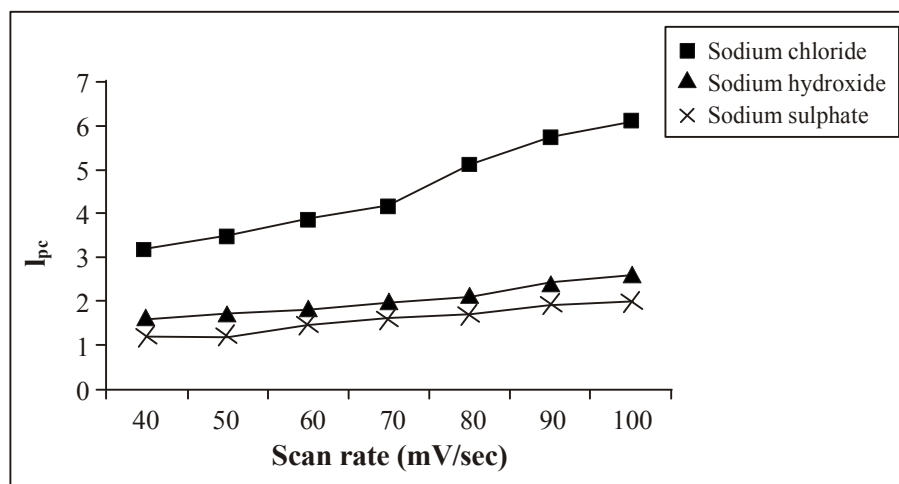
Fig. 1: Plots of I_{pa}/I_{pc} vs scan rate in different sodium salts as supporting electrolytes

The ratios of cathodic peak current (I_{pc}) and the square root of scan rate ($V^{1/2}$), for different supporting electrolytes are given in Table 3.

Table 3: Ratio of cathodic peak current and square root of scan rate (I_{pc} vs $V^{1/2}$)

S. No	Scan Rate (mV/sec)	$V^{1/2}$	1M NaCl	1M NaOH	1M Na ₂ SO ₄
1.	40	0.200	3.2	1.6	1.2
2.	50	0.233	3.5	1.7	1.2
3.	60	0.244	3.9	1.8	1.5
4.	70	0.264	4.2	2.0	1.6
5.	80	0.282	5.1	2.1	1.7
6.	90	0.300	5.7	2.4	1.9
7.	100	0.316	6.1	2.6	2.0

The plots of I_{pc} vs $V^{1/2}$ for different sodium salts as supporting electrolytes are given in Fig. 2. The plots yield almost horizontal lines except in NaCl.

**Fig. 2: Plots of I_{pc} vs $V^{1/2}$ in different sodium salts as supporting electrolytes**

All the above mentioned data indicate conclusively that the reduction of Pb (II) in the different sodium salts as supporting electrolytes is reversible at a mercury electrode. The value of ΔE is slightly higher than required for the two electron change reaction and increases slightly on increasing the scan rates. Since the condition for the anodic reverse sweep; is not the same as for initial cathodic sweep, there occurs a small anodic shift of

oxidation wave. Thus, separation of peak potentials would be slightly greater than that predicted from equation $\Delta E_p = 57/n$ mV.

The observed scan rates dependence on ΔE seems to be due to amalgam formation⁸. The fact that the peak height, peak potential, inflexion potential and the shape of wave are influenced by scan rates, indicates that amalgam formation results in considerable complexity⁹. Since there is a linear relationship between the height of cathodic peak current and square root of scan rate, it is concluded that the reduction process is diffusion controlled. Also cathodic and anodic peak potentials are more negative in NaCl and Na₂SO₄. This indicates the complexing tendency of chloride and sulphate ions with Pb (II)¹⁰.

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