STUDY OF Zn (II) IN DIFFERENT SODIUM SALTS AS SUPPORTING ELECTROLYTES USING CYCLIC VOLTAMMETRIC TECHNIQUE

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ABSTRACT

The reduction of Zn (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 Zn (II) is reversible.

Key words: Zinc, Sodium chloride, Sodium sulphate, Sodium nitrate.

INTRODUCTION

On the basis of theory of stationary electrode voltammetry as proposed by Nicholson and Shain[1], 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 couple[2] 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 an irreversible system[3], 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 voltammagrams.

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

EXPERIMENTAL

Cyclic voltammaograph 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 de-aeration and maintaining inert atmosphere over the test solution. All the experiments were carried out at 25 ± 0.1°C.

Reagent grade chemicals and triple distill water was used for all experiments. The concentration of Zn (II) ion was kept at 1×10^{-3} M, while supporting electrolytes used were sodium chloride (NaCl), sodium nitrate (NaNO$_3$) or sodium sulphate (Na$_2$SO$_4$) and their concentration was 1M.

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 –1.40 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 Zn (II) in different sodium salts as supporting electrolytes (in mV vs Ag-AgCl electrode)

Scan rates (mV/sec)	1 M NaCl			1 M NaNO₃			1 M Na₂SO₄		
	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p
40	-1.55	-0.99	56	-1.04	-0.99	50	-1.07	-0.99	80
50	-1.55	-0.99	56	-1.04	-0.97	70	-1.07	-0.99	80
60	-1.55	-0.99	56	-1.04	-0.99	50	-1.07	-0.99	80
70	-1.55	-0.99	56	-1.03	-0.97	60	-1.07	-0.99	80
80	-1.75	-1.00	75	-1.04	-0.99	50	-1.07	-0.98	90
90	-1.75	-1.00	75	-1.03	-0.98	50	-1.08	-0.98	90
100	-1.60	-1.00	60	-1.04	-1.99	50	-1.08	-0.98	100

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, NaNO₃, 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 is bit higher than the reported half-wave potential values of Zinc (-1.14 V vs SCE) in NaCl whereas they agree fairly with the half-wave potential of the medium in NaNO₃ and Na₂SO₄, respectively.

It is further noted that ΔE increases on increasing the scan rates in all supporting electrolytes. Hence, reduction of Zn (II) is not fully reversible in presence of sodium salts (NaCl, NaNO₃ and Na₂SO₄). However, the value of E_{pc} and E_{pa} are more negative in NaCl and NaNO₃ as supporting electrolyte than in Na₂SO₄.

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, where the values of I_{pa}/I_{pc} are also recorded.

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

Scan rates (mV/sec)	1 M NaCl			1 M NaNO$_3$			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}
40	1.15	2.4	2.08	2.3	4.8	2.08	1.4	3.7	2.64
50	1.21	2.45	2.02	2.4	4.9	2.04	1.7	3.85	2.26
60	1.35	2.5	1.85	2.8	5.0	1.78	2.2	4.3	1.95
70	1.50	2.7	1.80	2.9	5.1	1.75	2.5	4.7	1.88
80	1.60	3.1	1.93	3.4	5.2	1.52	2.9	5.2	1.79
90	1.70	3.2	1.88	3.5	5.3	1.51	3.0	5.3	1.76
100	1.90	3.4	1.78	3.7	5.4	1.45	3.1	5.4	1.74

It is seen that the ratio 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.
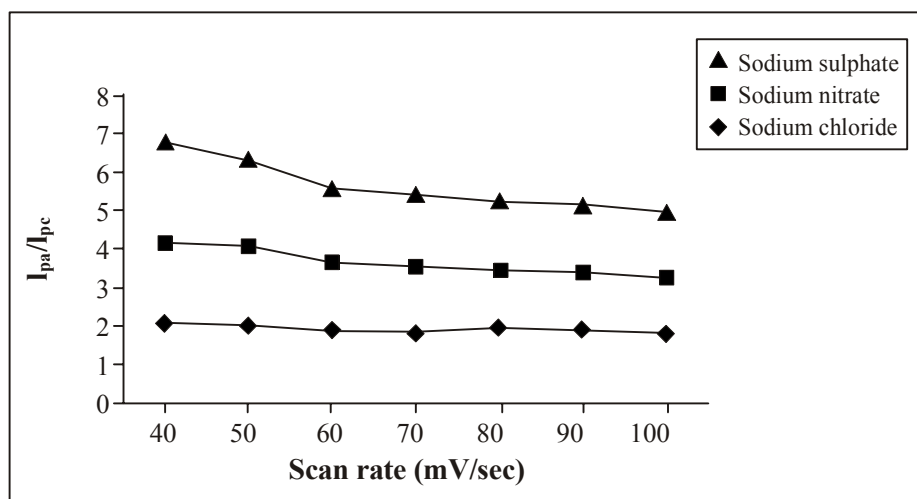

Fig. 1: Plots of l$_{pa}$/l$_{pc}$ vs scan rate (in mV) in different sodium salts as supporting electrolytes

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 $V^{1/2}$)

Scan rate (mV/sec)	$V^{1/2}$	1M NaCl	1M NaNO$_3$	1M Na$_2$SO$_4$
40	0.200	1.15	2.3	1.4
50	0.233	1.21	2.4	1.7
60	0.244	1.35	2.8	2.2
70	0.264	1.50	2.9	2.5
80	0.282	1.60	3.4	2.9
90	0.300	1.70	3.5	3.0
100	0.316	1.90	3.7	3.1

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 case of NaCl.
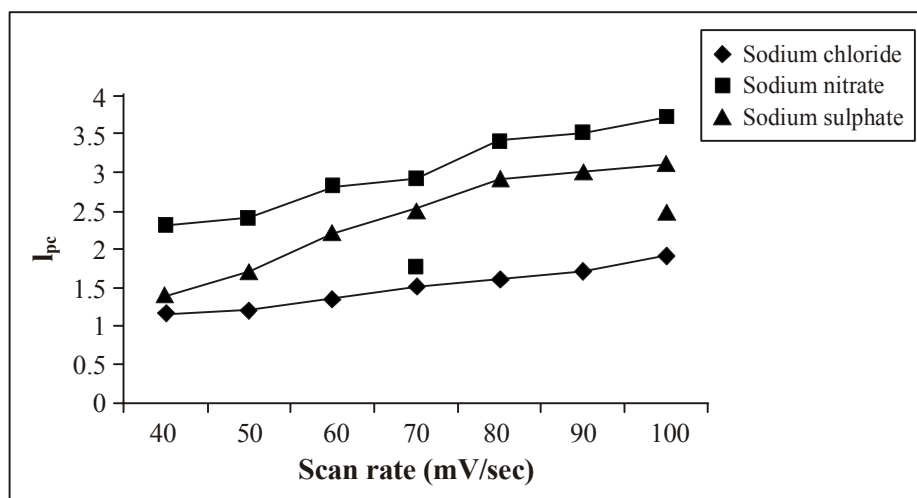
Fig. 2: Plots of l$_{pc}$ vs $V^{1/2}$ in different sodium salts as supporting electrolytes

Reduction of Zn (II) at hanging mercury drop electrode (HMDE) is influenced by the nature of the medium. From the data given above, it appears conclusively that the reduction of Zn (II) in the different sodium salts as supporting electrolytes is not fully reversible at a mercury electrode. In all, these peak current ratio (I_{pa}/I_{pc}) is much higher than unity. Further reduction of Zn (II) approached reversibility at very low scan rates.

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 formation[8]. The fact that the peak height, peak potential, inflexation potential and the shape of wave are influenced by scan rates, indicates that amalgum formation results in considerable complexity[9]. 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 as compared to $NaNO_3$ and Na_2SO_4. This indicates the complexing tendency of chloride ions with Zn (II).

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