Int. J. Chem. Sci. : 2 (4), 2004, 617–621

CYCLIC VOLTAMMETRY OF Cd (II) IN DIFFERENT SODIUM SALTS AS SUPPORTING ELECTROLYTES

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ABSTRACT

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

Key word : Cadmium, Cyclic Voltammetry, HDME

INTRODUCTION

On the basis of the theory of stationary electrode voltammetry 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 a irreversible system[3], then peak to peak distance is large and for reversible systems peak to peak distance is small.

The effect of a chemical reaction on the voltammetric wave will depend on its rate of reaction as compared with the time required to perform the experiment. Taking reversible succeeding 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 Cd(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 ± 0.1°C.

Reagent grade chemicals were used in all the experiments. Triple distill water was used for all experiments. The concentration of Cd (II) ion was kept at 1.0×10^{-3} M, and the supporting electrolytes used were NaCl, $NaNO_3$, 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).

One of the criteria for reversibility is that $\Delta E_p = 57/n$ mV. It is clear from Table 1 that the reduction of Cd (II) is reversible in all the supporting electrolytes, since $\Delta E_p \sim 30$ mV in all the cases. It is further noted that ΔE_p remains unchanged on increasing the scan rate. However, the value of E_{pc} and E_{pa} are more negative in 1 M NaCl as supporting electrolyte as compared to $NaNO_3$ and Na_2SO_4.

Table 1: Potential values of Cd (II) in different sodium salts as supporting electrolytes

S.No	Scan Rates in mV/sec	1 M NaCl			1 M $NaNO_3$			1 M Na_2SO_4		
		E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p
1.	40	–0.670	–0.630	40	–0.610	–0.580	30	–0.630	–0.600	30
2.	50	–0.665	–0.630	35	–0.600	–0.570	30	–0.630	–0.600	30
3.	60	–0.660	–0.630	30	–0.610	–0.580	30	–0.630	–0.600	30
4.	70	–0.660	–0.630	30	–0.600	–0.570	30	–0.630	–0.600	30
5.	80	–0.660	–0.625	35	–0.610	–0.580	30	–0.630	–0.600	30
6.	90	–0.665	–0.630	35	–0.600	–0.570	30	–0.630	–0.600	30
7.	100	–0.660	–0.625	35	–0.610	–0.580	30	–0.630	–0.600	30

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 along with values of I_{pa}/I_{pc} .

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

S.No	Scan Rates in mV/sec	1 M NaCl			1 M $NaNO_3$			1 M Na_2SO_4		
		I_{pa}	I_{pc}	I_{pa}/I_{pc}	I_{pa}	I_{pc}	I_{pa}/I_{pc}	I_{pa}	I_{pc}	I_{pa}/I_{pc}
1.	40	2.80	1.05	2.66	3.50	1.60	2.18	2.70	1.20	2.25
2.	50	2.95	1.20	2.45	3.50	1.70	2.05	2.80	1.45	1.93
3.	60	3.05	1.40	2.17	3.70	1.92	1.92	3.00	1.50	2.00
4.	70	3.15	1.55	2.03	3.80	2.10	1.80	3.15	1.65	1.90
5.	80	3.25	1.60	2.03	3.90	2.32	1.67	3.30	2.00	1.65
6.	90	3.30	1.75	1.88	4.00	2.45	1.63	3.40	2.10	1.61
7.	100	3.45	1.95	1.76	4.10	2.70	1.51	3.50	2.30	1.54

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 Figure 1. The ratio 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 $NaNO_3$	1M Na_2SO_4
1.	40	20.0	1.05	1.60	1.20
2.	50	23.3	1.20	1.70	1.45
3.	60	24.4	1.40	1.92	1.50
4.	70	26.4	1.55	2.10	1.60
5.	80	28.2	1.60	2.32	2.00
6.	90	30.0	1.75	2.45	2.10
7.	100	19.5	1.95	2.70	2.30

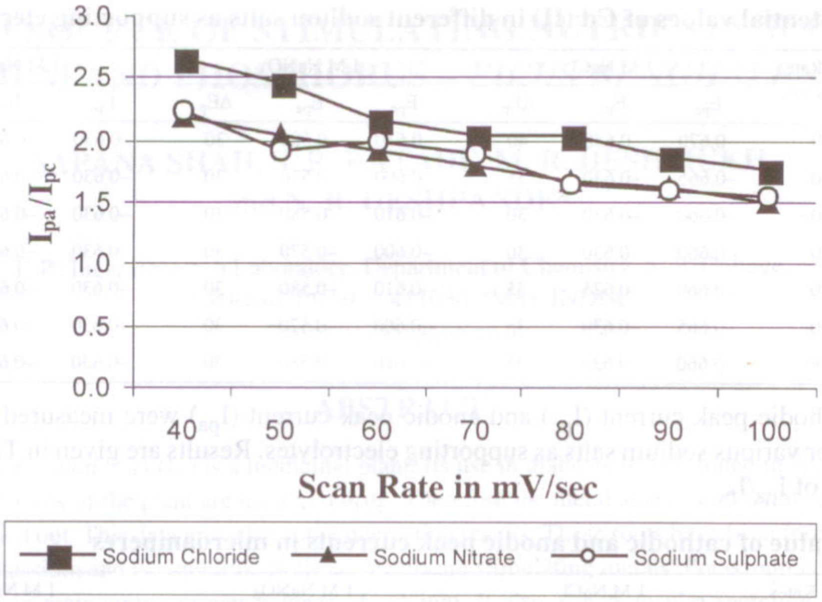

Figure 1. Plots of I_{pa} / I_{pc} vs scan rate mV/sec in different sodium salts as supporting electrolytes

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

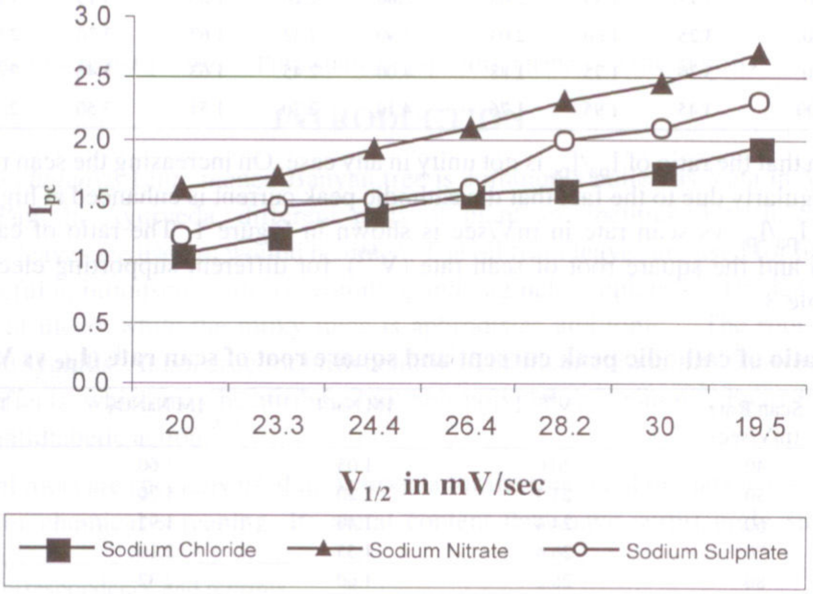

Figure 2. Plots of I_{pc} / $V_{1/2}$ in different sodium salts as supporting electrolytes

All the above mentioned data indicate conclusively that the reduction of Cd (II) in the different sodium salts as supporting electrolytes is reversible at a mercury electrode. 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 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 Na_2SO_4. This indicates the complexing tendency of chloride and sulphate ions withCd (II)[10].

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Accepted : 12.1.2004