POTENTIOKINETIC STUDIES ON CORROSION INHIBITORS

S. N. PANDEY, S. K. ROY, KANHAYA SINGH *and* K. N. PANDEY

Defence Materials & Stores Research & Development Establishment, Kanpur, India

Electrochemical methods, especially potentiostatic technique, are extensively being used by corrosion scientists to evaluate the corrosion inhibitors and also to study the possible mechanism of corrosion and inhibition processes. Potentiokinetic technique, which is a modification of the above has also been used with great advantage as it is less time consuming, although little more complicated than the former.

In order that these techniques can be successfully used as a testing tool, it is necessary to understand the effect of many variable factors, which may affect the results and hence its interpretation. An attempt has been made in the present paper to discuss some of the factors especially sweep rate connected with the potentiokinetic studies on the corrosion inhibitors for mild steel.

Potentiokinetic anodic polarisation studies of mild steel were carried out in (*a*) different concentrations of sodium benzoate, sodium nitrite and potassium chromate containing 0.01N sodium chloride solutions of different sweep rates, ranging from 10mV to 200mV/min and (*b*) in 1.0 per cent sodium nitrite solution at a constant sweep rate of 200mV/min in presence of various concentrations of sodium chloride with changing pH of the solutions. The effect of aeration and deaeration have also been studied in both the sets of experiments.

The sweep rates have been found to have a pronounced effect on the domain of passivity for mild steel in presence of both sodium benzoate and potassium chromate solution. This was found to widen with increase in sweep rates. This effect was more marked when the experiments were caried out at increasing concentrations and in case of potassium chromate solution this effect was more than in benzoate and nitrite.

Increase in the domain of passivity in deaerated condition was found to be in the following decreasing order :

(*a*) Potassium chromate (*b*) Sodium nitrite and (*c*) Sodium benzoate. In case of aeration this order changed to : Sodium benzoate, followed by nitrite and then potassium chromate.

The magnitude of the passive CD changed with the conditions of aeration, deaeration and concentrations of the inhibitive anions. In aerated solution this was the lowest in sodium benzoate and the highest in potassium chromate solution. In deaerated condition it was reversed. Sweep rates were observed to have no effect on the passive CD.

The results so obtained by potentiokinetic polarisation studies have been compared by plotting time-potential curves, using galvanostatic technique at different CD, corresponding to that as obtained in the above experiments.

Metal loss for mild steel for different periods were determined to substantiate the results obtained by electrochemical techniques. The efficiencies of the inhibitors as obtained from the results of our studies in deaerated solution seem to be as $K_2CrO_4 > NaNO_2 > C_6H_5COONa$ and in aerated solution $C_6H_5COONa > NaNO_2 > K_2CrO_4$.

Experiments were carried out to study the effect of pH, concentration of sodium chloride and aeration and deaeration at 200mV/min constant sweep rate. It has been found that in case of 1.0 per cent sodium nitrite in distilled water, passivation could not be achieved in absence of oxygen, where the pH is less than 5.3. However, if aeration was introduced, this critical pH changed to 4.96. In presence of 0.01 per cent sodium chloride the critical pH for passivation was found to be 5.8 in absence of oxygen. On introduction of oxygen, this pH changed to 5.0.

Mechanism based upon the rate of transport of cations and anions has also been discussed in this paper.

Keywords : Potentiokinetics; Corrosion Inhibitors; Effect of Aeration

INTRODUCTION

ELECTROCHEMICAL methods, specially potentiostatic and galvanostatic techniques are extensively and successfully being utilised by corrosion scientists to evaluate the corrosion inhibitors and also to study the possible mechanism of corrosion and inhibition processes. Potentiokinetic technique which is a modification of potentiostatic technique has also been used with great advantage, it is at the same time rapid, reproducible, selective and interpretable. In this technique, the electrode potential is varied linearly with time yielding a continuous current-potential relationship.

The potentiokinetic method (Pourbaix *et al.*,1963; Epelboin *et al.*,1962; Prazak, 1963; Jones *et al.*, 1965; Little Wood, 1963; Greene & Leonard, 1964; and Pourbaix, 1965) and the step potential method has been used by several workers (Edeleanu, 1958; Greene, 1960; and Makrides, 1961). These two methods have been compared on metals showing vigorous passive behaviour. Greene found that equilibrium current-potential diagrams derived by the two methods were very similar, provided the potential range was traversed slowly enough. However, systematic studies have not been carried out for finding out the effect of the rate of linear variation of potential on the active-passive behaviour as depicted by current-potential curves. Srinivasan and Gileadi (1966) analysed theoretically the relationship between current potential curves obtained experimentally and the sweep rates.

In order that this technique can be successfully used as testing tools, it is necessary to understand the effect of many variable factors, which may affect result and hence their interpretation. Therefore, it has been thought to study the effect of the parameters, side by side and the effect of pH of the electrolytes on different corrosion inhibitors in terms of active passive transition phenomenon from the anodic polarisation diagrams of mild steel. This paper presents some of the results of potentiokinetic studies on the different corrosion inhibitors for mild steel in aqueous media as effected by sweep rate.

<center>EXPERIMENTAL</center>

Apparatus

Potentiokinetic anodic polarisation of mild steel was carried out by (*a*) Wenking potentiostat and (*b*) Electrochemograph. In the former, the potential was imposed on the working electrode through stepping motor potentiometer coupled with Wenking potentiostat. The potential was varied from 10mV to 200mV/min and the resulting current was recorded through an electrometer connected with a potentiometric recorder. Conventional Electrochemical Cell was used for the determination of polarisation curves. The mild steel electrode was placed vertically in the central portion of the cell. A luggin capillary filled with the experimental solution led through a tap to the electrochemical cell just 1mm away from the working electrode. The other end of the capillary was kept in a glass beaker also filled with the experimental solution in which the saturated calomel electrode was placed. Platinum auxiliary electrode was placed inside the electrochemical cell just near the working electrode through 3G sintered tube fitted with standard joint inside the cell. (*b*) Electrochemograph was used for getting the polarograms and anodic polarisation of mild steel in different experimental solutions. In this case, the rate of increase of potential was 200mV/min fixed. The total potential range covered was —800 to +950mV. Saturated calomel was used both as reference and auxiliary electrode in this set of experiment.

Solution

LR BDH grade sodium benzoate, AR BDH sodium nitrite and GR potassium chromate were used to prepare 0.01, 0.05 and 0.10N concentrations of the three inhibitors for mild steel in presence of 0.01N AR grade sodium chloride solution in double distilled water for the set (*a*) experiments. In the set (*b*) experiments AR BDH sodium nitrite was used to prepare 1.0 per cent (0.14N approx.) solution, in double distilled water in presence of 0.01 per cent (approx. 0.02N) sodium chloride with changing *p*H of the solution. The *p*H of the solution was adjusted by adding sodium hydroxide or acetic acid as per requirement of the experiment. In all the experiments, one sq. cm area of polished and degreased mild steel specimen was used. The deaeration of the experimental solution was made by passing dry and pure nitrogen gas bubbles into the electrochemical cell through fine pores of glass bulb joined by standard joint in the cell. Aeration was made by passing dry air.

<center>RESULTS AND DISCUSSIONS</center>

(*a*) *Effect of Sweep Rates on the Polarisation Behaviour of Mild Steel in Different Inhibitor Solutions*

Potentiokinetic anodic polarisation of mild steel has been made in aerated and deaerated solution of different concentrations of sodium nitrite, sodium benzoate and potassium chromate solution containing 0.01N sodium chloride at 10mV to 200mV/min sweep rates. All the polarisations of mild steel were made after the potential of the mild steel electrode in the respective inhibitor solutions attained steady state value.

Some of the representative polarisation curves at different sweep rates are shown in Figs. (1-6). The values of breakdown potentials of passive film formed on mild steel as affected by different inhibitors by sweep rates are computed from the polarisation curves and are given in Table I.
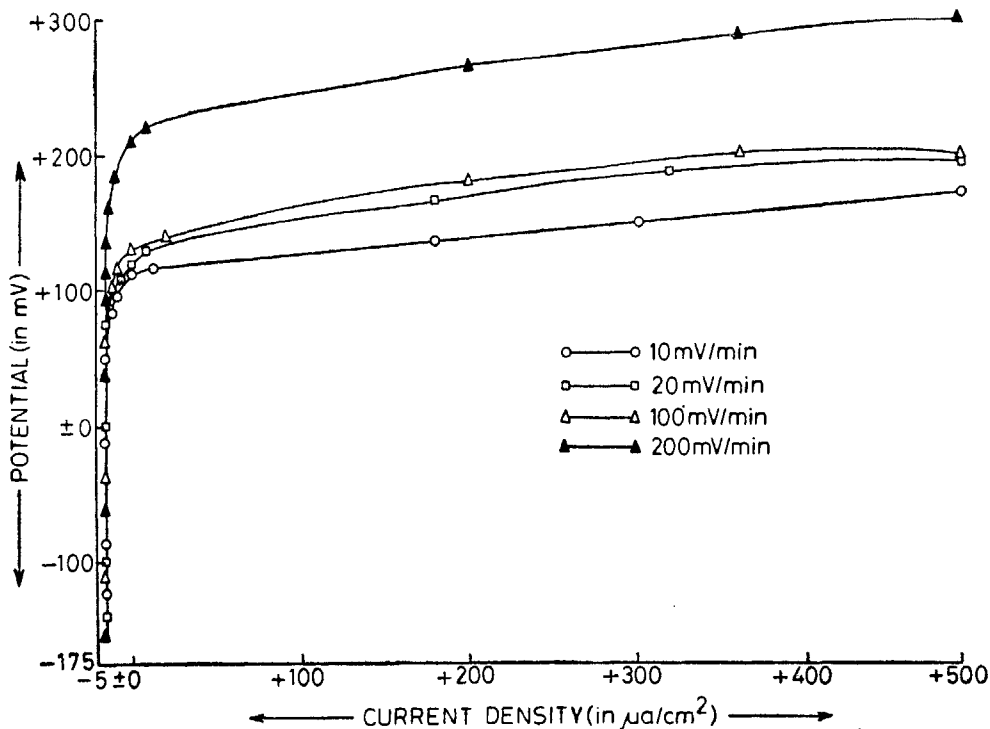

FIG. 1.

TABLE I

The breakdown potentials of the passive film formed on mild steel in different inhibitors containing 0.01N NaCl at different sweep rates in aerated and deaerated environments

A—AERATED ENVIRONMENT

Sweep Rates/min	Sodium Benzoate		Sodiuum Nitrite		Potassium Chromate	
	0.05N	0.1N	0.05N	0.1N	0.05N	0.1N
10mV	+ 116mV	+ 205mV	+ 176mV	+ 210mV	+ 120mV	+ 265mV
20mV	+ 124	+ 240	+ 184	+ 215	+ 140	+ 280
50mV	+ 132	+ 330	+ 196	+ 220	+ 180	+ 300
100mV	+ 140	+ 360	+ 204	+ 225	+ 188	+ 320
200mV	+ 224	+ 390	+ 230	+ 240	+ 220	+ 340

B—DEAERATED ENVIRONMENT

Sweep Rates/min	Sodium Benzoate		Sodium Nitrite		Potassium Chromate	
	0.05N	0.1N	0.05N	0.1N	0.05N	0.1N
10mV	+ 120mV	+ 300mV	+ 220mV	250mV	+ 180mV	+ 360mV
20mV	+ 140	+ 320	+ 224	+ 260	+ 200	+ 400
50mV	+ 172	+ 332	+ 228	+ 275	+ 210	+ 425
100mV	+ 180	+ 350	+ 232	+ 290	+ 220	+ 440
200mV	+ 188	+ 380	+ 244	+ 308	+ 240	+ 480

(*i*) *Sodium Benzoate*: The values of passivity breakdown potential values for mild steel in 0.05N and 0.1N sodium benzoate solutions both under aerated and deaerated conditions as effected by different sweep rates are given in Table I. It is observed that under aerated conditions increase in breakdown potential values at sweep rates between 10mV to 100mV/min was not very significant and it changed from 116 to +140mV between this range. However, the potential of mild steel electrode abruptly increased to +224mV, when the sweep rate was increased from 100mV/min to 200mV/min. Such sudden increase in breakdown potential was found to be absent in deaerated 0.05N solution. The difference of 68mV in 0.05N deaerated benzoate
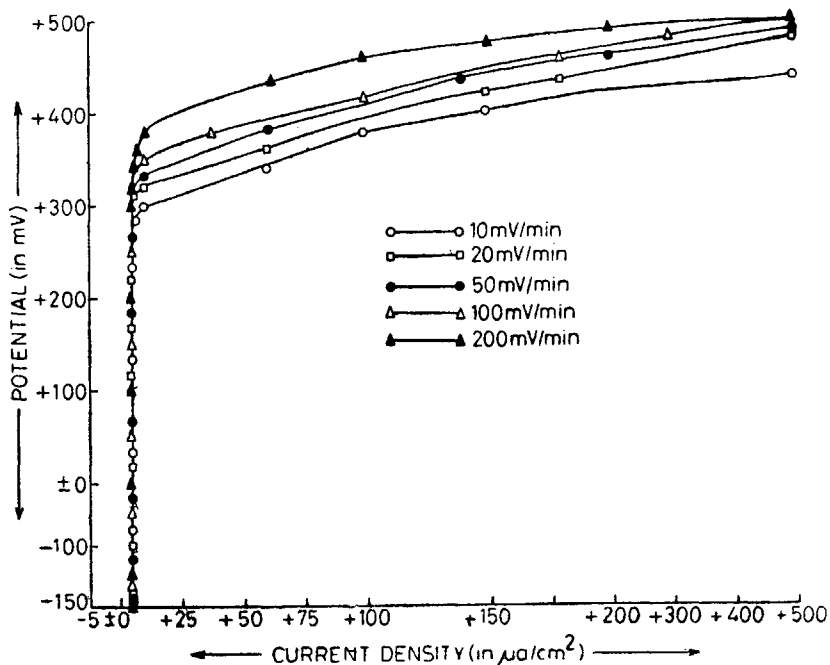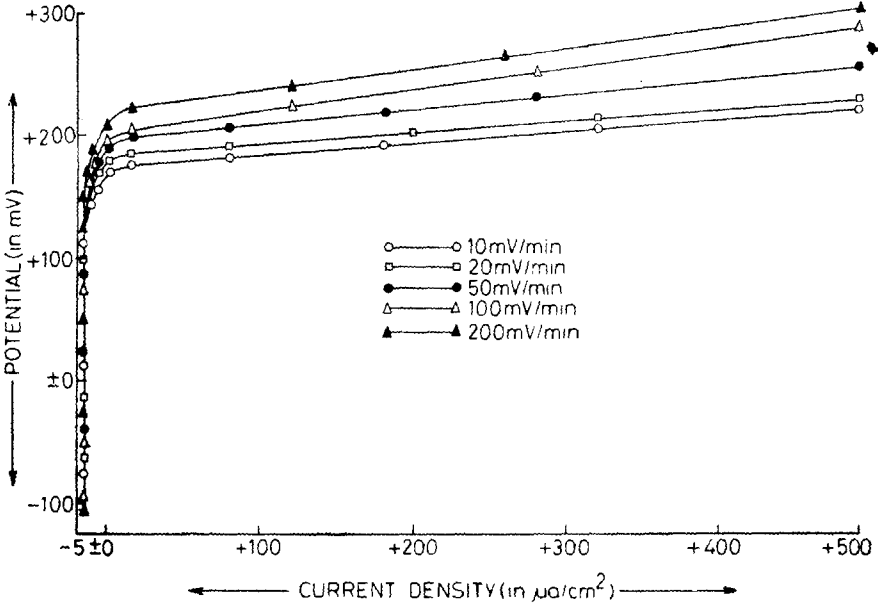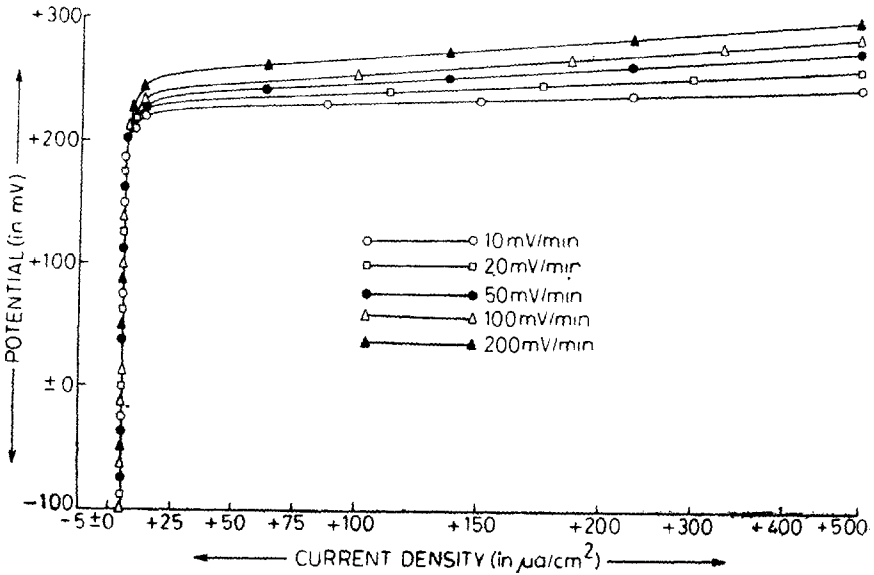

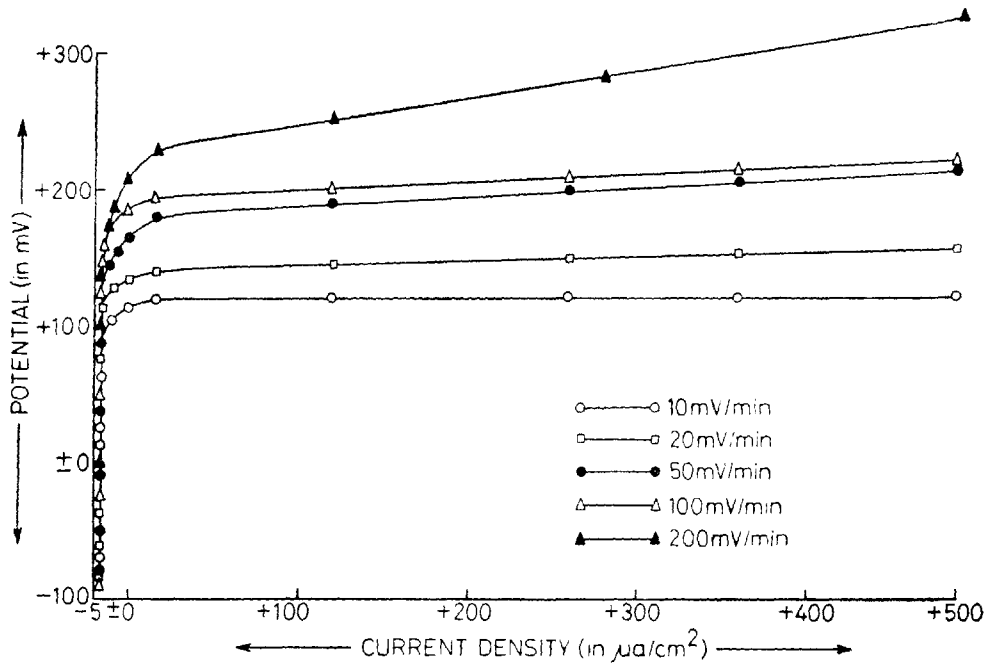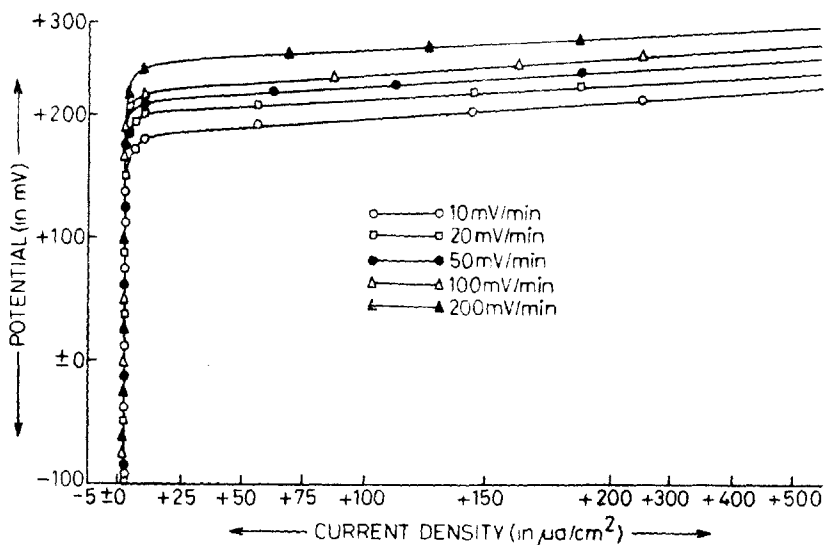FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

FIG. 6.

solution was observed against 108mV in aerated solution at the lowest and the highest sweep rates, which indicates that under aerated condition the domain of passivity widened more with the increase in sweep rates than in deaerated solution of 0.05N sodium benzoate solution.

In aerated 0.1N solution the abrupt increase in breakdown potential was observed when the sweep rate was increased above 20mV/min. These values were +205 and +240mV at 10 and 20mV/min respectively, which suddenly increased to +330mV at 50mV/min and finally the increase was gradual and at 200mV/min it was found to be +390mV. In deaerated solution this trend was absent as observed in lower concentration. However, these values were more +ve and found to vary between +300 and +380mV giving a difference of 80mV against 185mV in aerated solution between the lowest and the higest rate.

(*ii*) *Sodium Nitrite* : In aerated sodium nitrite solution at 0.05N concentration the passivity breakdown potentials increased at regular interval at the rate of 8 to 12mV from initial value of +176 at 10mV/min to +204 at 100mV/min which changed to +230mV at 200mV/min sweep rate, whereas these values were observed to change from +220 to +244 in deaerated solution. When the concentration was increased to 0.1N, almost same trend was followed in aerated solution and the breakdown potentials were found to vary between +210 and +240 at the lowest and the highest sweep rates respectively.

In deaerated 0.1N sodium nitrite solution the breakdown potential values were found to be higher which were between +250 and +308mV when the sweep rates were changed from 10mV to 200mV/min and the effect of the sweep rates have been found to be more pronounced under deaerated condition. In general, the results indicate that with the increase in concentration from 0.05 to 0.1N, the sweep rates did not have much influence on the passivity breakdown potentials, and subsequently on the domain of passivity as observed in sodium benzoate solution. However, these values were more +ve in deaerated solutions.

(*iii*) *Potassium Chromate* : The sweep rates have been found to have a marked effect on the domain of passivity as well as on the rate of increase of breakdown potentials in potassium chromate solutions containing 0.01N sodium chloride as it was observed in benzoate. In aerated 0.05N potassium chromate solution the break-down potentials were found to vary between +120mV and 220mV at the lowest and the highest sweep rates respectively. When the concentration was increased to 0.1, these values were +265mV and +340mV; with the increase in concentration of the inhibi-tive anions more +ve values of breakdown potentials were obtained. However, on deaeration of the solutions the extent of increase in breakdown potentials at the different sweep rates became +ve than in aerated solution.

In 0.05N deaerated solutions, the breakdown potentials changed from +180mV at 10mV/min to +240 at 200mV/min sweep rate. In 0.1N deaerated solution, the values were signifiably higher than in any other inhibitive anions. The increase of sweep rates had considerable effect as to increase the domain of passivity and also subsequently the values of breakdown potentials. The passivity breakdown

potentials were found to change from an initial value of +360 to +480mV at the max sweep rate of 200mV/min.

The magnitude of the passive current density changed with the conditions of aeration, deaeration and concentrations of the inhibitive anions. In aerated solution this was the lowest in sodium benzoate solution and the highest in potassium chromate solution. In deaerated condition it was reversed. Sweep rates were observed to have no effect on the passive current density.

(b) *Effect of pH in deaerated 1.0 per cent (0.14N) Sodium Nitrite Solution*

Anodic polarisation curves of mild steel under deaerated condition are shown in Fig. 7 curves (a), (b), (d), (e), (f) and (g) for pH values of 4.96, 5.30, 5.74, 6.00,
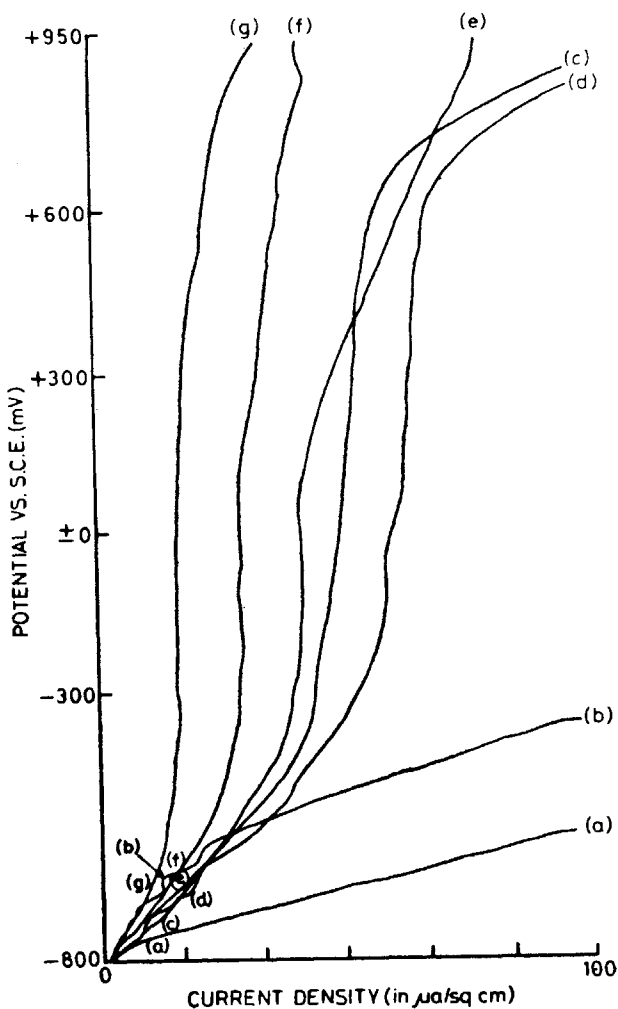

FIG. 7.

9.42, 9.80 and 11.12 respectively. This is due to curves (*a*) and (*b*) which are straight lines indicating complete absence of chemical polarisation. Remaining curves are of the same nature. The current density and the potential at the first break at which current ceases to increase over a considerable range of positive potential scan is called critical current density and critical potential for passivation under this condition. As *p*H was increased beyond 6.0 polarisation, curves (*e*) to (*g*) were obtained. The critical potentials for passivation became more negative and the critical current density decreased considerably but the domain of passivity became narrower as *p*H was decreased. It is thus seen that in solutions having *p*H below 5.3, passivation of mild steel is not achieved in deaerated solution. This indicates that critical *p*H for passivation lies between 5.3 and 5.7. As pointed out by Matsuda and Uhlig (1964) this becomes possible as nitrite decomposes at low *p*H values.
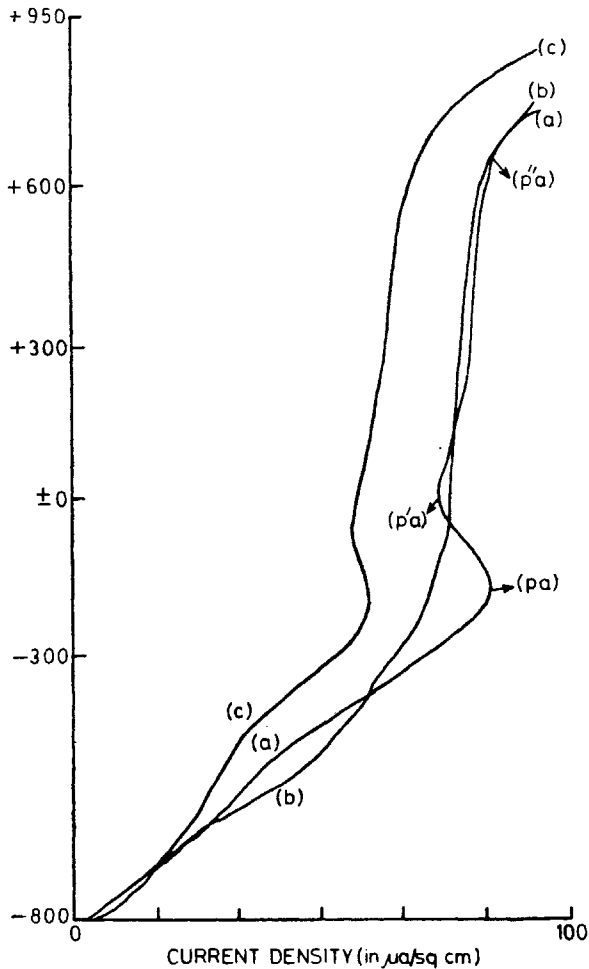

FIG. 8.

Effect of pH in Aerated Solution

Polarisation curves (a) to (c) in Fig. (8) were obtained in aerated solutions of NaNO₂ at pH 4.96, 5.04 and 5.3 respectively. Introduction of aeration in a solution of pH 4.96 changed the nature of the curve. Instead of a straight line it shows [curve (a)] considerable polarisation. The polarisation behaviour of mild steel under these conditions indicate that as the oxygen concentration has been stabilized, process of secondary passivation is induced. These results have helped in finding out an important fact that nitrite at lower pH can induce passivity to mild steel in presence of sufficient amount of oxygen only Pandey (1966) has reported that even in neutral solution nitrite decomposes if oxygen is absent which results in impairing the efficiency of this inhibitor. At higher pH the absence of oxygen affects the process very little, since NaNO₂ is not decomposed much under these conditions and the role of nitrite becomes complimentary to that of oxygen provided sufficient amount of nitrite is present.
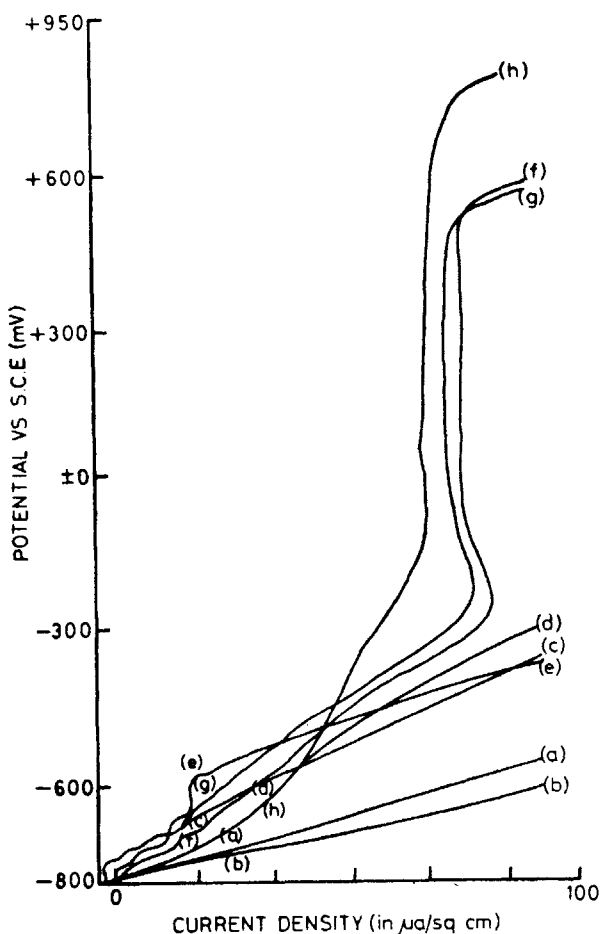

FIG. 9.

Combined Effect of NaCl and pH

The combined effect of different pH (4.96 to 5.8) and 0.01 per cent (.02N approx.) sodium chloride on the anodic polarisation of mild steel in 1.0 per cent (0.14N) sodium nitrite solution is shown in Fig. 9 curves (*a*) to (*h*). Polarisation curves both under aerated and deaerated solutions of 4.96 pH are straight lines. The straight line curves were also obtained where pH of the solutions was increased upto 5.7, but the solutions were deaerated. However, with the aeration of the solution, polarisation of mild steel was observed even at lower pH at 5.00. Solution in increasing the pH to 5.74 anodic polarisation became possible even under deaerated nitrite solution in presence of 0.01 per cent NaCl. It has already been explained that $NaNO_2$ can induce passivity in lower pH if oxygen is present, but presence of Cl^- ion has got so much stimulating effect on dissolution process that oxygen is unable to promote inhibition unless pH is increased further. The presence of Cl^- ion has increased the critical pH value for passivation of mild steel by $NaNO_2$ in absence of oxygen. This critical pH was 5.74 as compared to 5.3 in solutions of only 1.0 per cent (0.14N approx.) containing no Cl^- ion.

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