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# Inhibition of corrosion of Ni in HCl by acetylenic alcohols – Comparison of impedance and SACV

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The corrosion of nickel in hydrochloric acid solutions and inhibition by propargyl alcohol (PA), 3 butyn-2-ol (BO), 2-methyl 3-butyn-ol (MBO) and 2 butyn-1:4 diol (BD) was studied.

**Key words: Corrosion, nickel, acetylenic alcohol, impedance**

## INTRODUCTION

Acetylenic alcohols are known to be inhibitors for the corrosion of pure nickel and iron in hydrochloric acid solutions [1–3]. This paper presents the results obtained from small amplitude cyclic voltammetric studies and Faradaic impedance in 1 to 10N HCl solutions for the corrosion of nickel and inhibition by these alcohols.

## EXPERIMENTAL

Detailed description of electrode preparation, cell and small amplitude cyclic voltammetry (SACV) experimental set-up were given earlier [1]. The impedance measurements were made in the frequency range of 0.1 to 1 Kc/s using PAR impedance system Model 5206.

## RESULTS

Typical SACV for nickel in 1N acid is shown in Fig. 1. In presence of alcohols also, a similar type of behaviour is observed with decrease in magnitude of current. The hysteresis current also decreases with the addition of alcohols.

In order to obtain the true $R_p = (dE/d_i)$ values calculated from the slope of first cycle, forward scan are plotted against v and extrapolated to v=0, and the true $R_p$ at v=0 is taken for the calculation of $i_{corr}$. Secondly $1/R_d$ values ($R_d$=diagonal values) are plotted against v and extrapolated to v=0, and $1/R_d$ values at v=0, is taken as $1/R_p$ assuming $1/R_s$ is negligible. The hysteresis exhibited by the system between forward and reverse sweeps has been analysed to calculate the $C_{dl}$.

$$\% \text{ inhibition} = \left[\frac{(1/R_d) - (1/R_d')}{(1/R_d)}\right] \times 100$$

$$= \frac{(R_p - R_p')}{R_P} \times 100$$

where $R_p'$ and $(1/R_d')$ are values obtained at v=0 in

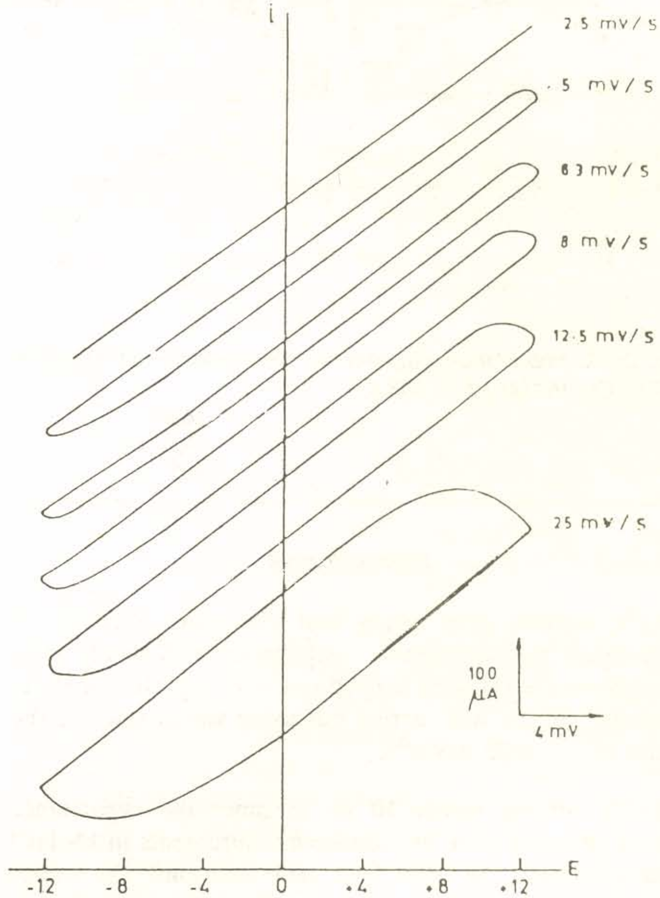


*Fig. 1: Typical SACV for nickel in 1N HCl*

presence of alcohols. Figure 2 presents impedance spectrum for nickel in 5N HCl containing alcohols. $R_s$ and $R_t$ values were obtained from the high frequency and low frequency values of the real part of the impedance. The frequency at which impedance of the system exhibits the maximum value was used to calculate the capacitance of the double layer. $R_t$ values with and without inhibitors were used to calculate the percentage inhibition.

$$\%\text{inhibition} = \frac{(C_{dl})_0 - (C_{dl})_I}{(C_{dl})_0} \times 100$$

$$= \frac{(1/R_t) - (1/R_t')}{(1/R_t)} \times 100$$

$(C_{dl})_0$, $(1/R_t)$ are values for acid and $(C_{dl})_I$ and $(1/R_t')$ for acid containing inhibitors. Table I presents the comparison of $C_{dl}$ and % inhibition obtained by the two methods.

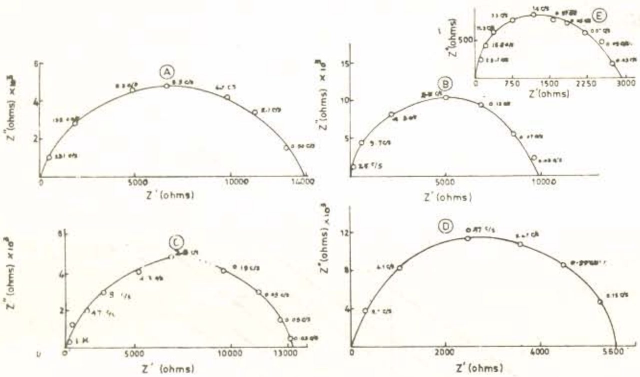


*Fig. 2: A. Impedance diagram for the corrosion of nickel in 5.0N HCl+10$^{-2}$M PA at 303 K*

*B. ,, ,, ,, MBO*

*C. ,, ,, ,, BO*

*D. ,, ,, ,, BD*

TABLE–I: Comparison of $C_{dl}$ and inhibition efficiencies obtained from two methods

| Concentration of inhibitor ($10^{-2}$M) | SACV | | | Impedance | | |
|---|---|---|---|---|---|---|
| | (dE/dl) $v \to 0$ | ($1/R_d$) $v \to 0$ | $C_{dl}$ ($\mu$F) | ($1/R_p$) method | $C_{dl}$ method | $C_{dl}$ $\mu$F |
| 1.0N HCl | – | – | 520 | – | – | 185.0 |
| PA | 50 | 50 | 280 | 95 | 96.5 | 7.5 |
| MBO | 53 | 40 | 200 | 96 | 94.4 | 10.5 |
| BO | 53 | 60 | 240 | 96.5 | 96.5 | 6.5 |
| BD | 27 | 20 | 440 | 87 | 83 | 32.0 |
| 5.0N HCl | – | – | 300 | – | – | 290 |
| PA | 76 | 56 | 30 | 95 | 80 | 10 |
| MBO | 81 | 56 | 65 | 87 | 75 | 25 |
| BO | 80 | 55 | 89 | 80 | 72 | 37.5 |
| BD | 77 | 60 | 59.5 | 23 | 50 | 150 |
| 10.0N HCl | – | – | 125 | – | – | 85.3 |
| PA | 69 | 50 | 37.5 | 86 | 98 | 11.7 |
| MBO | 41 | 33 | 37.5 | 97 | 97 | 2.3 |
| BO | 41 | 50 | 9 | 84 | 94 | 13.3 |
| BD | 46 | 50 | 37.5 | 16 | 66 | 71.5 |

## DISCUSSION

SACV method gave nearly half the value obtained by impedance measurements. Impedance and steady state measurements [1] were carried out over a period of thirty minutes. SACV was carried out using sweep rates of the order of 2.5 to 25 mV.s$^{-1}$.

SACV offered nearly 10 to 15 times the capacitance values obtained from impedance measurements in 1N HCl acid solutions. In 10N HCl acid solutions, the values are nearly of the same order. Presence of inhibitors decreased the capacitance and MBO exhibited maximum decrease. In SACV, though v are moderately faster, the potential range in which they are scanned are very narrow. The higher capacitance values obtained during the time interval is entirely due to pseudo capacitance caused by adsorbed NiCl [1] and presence of alcohols decreased these values. In various examples of impedance diagram observed, depressed semicircles appeared whose centre was below the real axis. This phenomenon is well in homogeneous media studies where the cole-cole dispersion is the rule for dielectric relaxation and is explained by a repartition of the time constants of the processes around a central value. The repartition of the time constant is generally explained either by the roughness of the electrode surface or by geometrical effects leading to a nonuniform repartition of the current density of the surface. As the roughness increases, a deviation of the impedance characteristics from the vertical and a decrease in the double layer capacitance were observed.

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