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Inhibitions Corrosion of Nickel in Perchloric Acid by mono-substituted Phenyl N-phenylcarbamates

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*Received August 8, 1989*

The use of some mono-substituted phenyl N-phenylcarbamates derivatives as corrosion inhibitors for nickel in 1M perchloric acid was studied by galvanostatic polarization. The inhibition appears to function through general adsorption isotherm. However, galvanostatic polarization data suggest that in the case of all seven inhibitors both anode are polarized under the influence of an external current. Electrocapillary measurements have also revealed that the tendency of the inhibitors tested to adsorb on metallic surface follows the same order of efficiency.

Introduction

The anodic dissolution of nickel in different acid solutions in the presence of organic and inorganic inhibitors have recently received considerable attention[1-13]. Polarization measurements afford information about the influence of inhibitors on the cathodic and anodic partial processes, in addition to the usual data they provide about corrosion rates.

Nitrogen containing organic corrosion inhibitors, which adsorb at the metal/solution interface and thus reduce the metal activity, have been investigated by many authors[14-16] using mild steel, zinc and aluminium substrates but very few studies have been made on nickel in acid solution, despite the fact that these N-containing organic molecules act as strong chelating ligand with nickel[17]. This paper describes studies of the adsorption of phenyl N-phenylcarbamate derivatives (1-7) on nickel surfaces and their effect on corrosion inhibition.
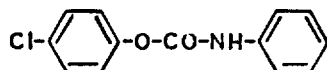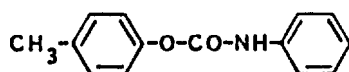
1-p-methoxyphenyl N-phenylcarbamate
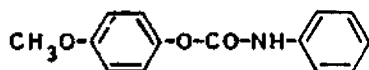
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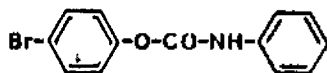
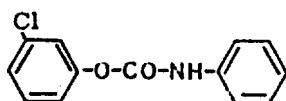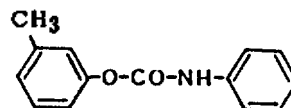3-p-chlorophenyl N-phenylcarbamate

4-p-methylphenyl N-phenylcarbamate
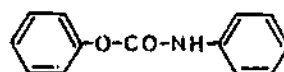

5-m-chlorophenyl N-phenylcarbamate

6-m-methylphenyl N-phenylcarbamate

7-phenyl N-phenylcarbamate

Experimental

Apparatus and Working Procedures. The chemical composition of the nickel wire (BDH grade) used was as follows: Al: 0.005, Co: 0.005, Cu: 0.005, Fe: 0.05, Mn: 0.005, Mg: 0.005, Ti: 0.005, Ni: rest. The wires were abraded mechanically with different grades of emery paper and were finally wet grinded with 4/0 polishing paper. The exposed circular area in each experiment was 0.20 cm^2. The wires, were thoroughly washed with distilled water and dried immediately prior to use.

For the polarization measurements a Galvanostat-Potentiostat (Amel 549) was used as a constant current source. A saturation calomel reference electrode with a luggin capillary tube and a platinum wire counter electrode were used. The corrosion potentials were recorded using a pH-mV meter (Tacussel Minisis 5000). All the measurements were made at 27 ± 1 °C. Corrosion currents were calculated from the measured polarization data by the method as described by Mansfeld.[18]

Preparation of Phenyl N-phenylcarbamates. A solution of the appropriate phenol (0.01 mol) in dry benzene (10 m*l*) was added to a solution of phenyl isocyanate (1.19 g, 0.01 mol). A catalytic quantity of pyridine (0.5 m*l*) was added and the solution was refluxed for 1 hr. On evaporation of the solvent in vacuo, the carbamate ester was precipitated in almost quantitative yield. It was collected and crystallized from chloroform-pentane to constant melting point. The structures of the compounds were identified by elementary, IR and NMR analysis. $HClO_4$ was of AR grade.

Results

The data obtained for the electrochemical and corrosion

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Table 1. Tafel Parameters During Acid Corrosion of Nickel in Presence of Inhibitor (3) at 27 ± 1 °C

Concentration M	E_{corr}, mV ± 5 mV	I_{corr} μA cm^{-2}	bc mV/decade ± 5 mV	ba mV/decade ± 5 mV	ΔG_{ads} K cal/mol^{-1}	Inhibition efficiency %
0.0	200	63.10	25.0	12.0	—	—
5×10^{-6}	200	39.81	28.3	10.0	9.4	36.9
1×10^{-5}	198	31.62	25.0	12.0	9.3	49.9
5×10^{-5}	196	13.18	20.0	5.0	9.1	79.1
1×10^{-4}	195	10.00	20.1	5.0	8.9	84.2
5×10^{-4}	193	7.94	20.0	10.0	8.1	87.4
1×10^{-3}	190	5.62	20.0	10.0	7.9	91.1

Table 2. Effect of Various Carbamates on Cathodic and Anodic Tafel Slopes Corrosion Current Density, Free Energy of Adsorption and Inhibitor Efficiency

Corrosive medium (1M HClO$_4$ + 10^{-5}M inhibitor)	E_{corr}, mV ± 5 mV	I_{corr} μA cm^{-2}	bc mV/decade ± 5 mV	bc mV/decade ± 5 mV	ΔG_{ads} K cal/mol^{-1}	Percent efficiency
HClO$_4$	200	63.10	25.0	12.0	—	—
7	200	56.39	25.0	12.0	8.0	10.6
6	200	51.51	28.3	10.0	8.4	18.4
5	200	46.30	26.0	11.0	8.7	26.6
4	198	40.40	27.0	12.0	9.0	36.0
3	198	31.62	25.0	12.0	9.3	49.9
2	198	26.11	40.0	10.0	9.5	58.6
1	195	22.39	43.3	10.0	9.7	64.5

behaviour of nickel in 1M HClO$_4$ solution in the absence and presence of monosubstituted phenyl N-phenylcarbamates in the concentration range 5×10^{-6}-1×10^{-3}M are given in Table 1. Corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic Tafel slopes, free energy change of adsorption process (ΔG_{ads}) and percent efficiency for nickel is solutions containing 10^{-5}M of mono–substituted phenyl N-phenylcarbamates are given in Table 2. These results show that E_{corr} of nickel in the presence of inhibitors is slightly shifted in the positive direction. This small shift (0–5 mV) indicates that these compounds are mixed type inhibitors (Figure 1) and that both cathodic and anodic partial processes are affected to nearly the same extent by the inhibition[19], so that inhibition takes place by simple blocking of the electrode surface with subsequent decrease of the area available to the respective partial processes. The approximately constant value of the cathodic and anodic Tafel slopes (bc, ba) in the absence and presence of inhibitor indicates that the mechanism of the reaction of HClO$_4$ with nickel metal is not affected by their presence, and suggests primary interface inhibition[20,21].

The degree of surface coverage (θ) for this type of inhibition is given by the equation:

$$\theta = \frac{i_{uninh} - i_{inh}}{i_{uninh}} \tag{1}$$

where i_{uninh} and i_{inh} and the uninhibited and inhibited corrosion currents respectively. These are determined by the in-
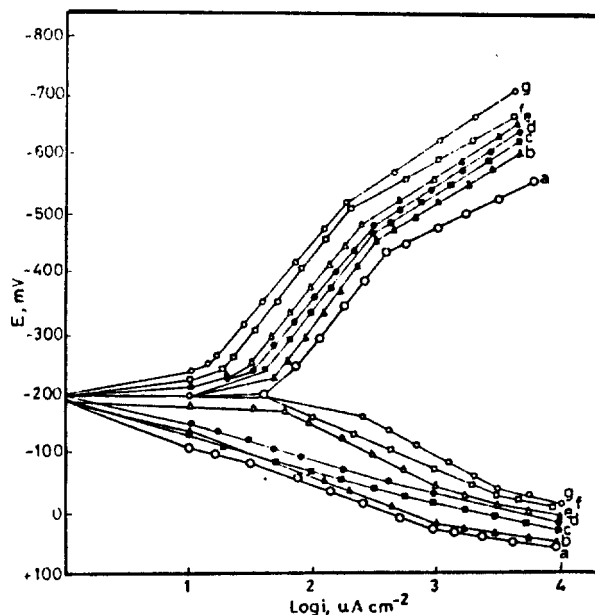
Figure 1. Galvanostatic polarization curves of nickel in 1M HClO$_4$ alone, and containing different concentrations of p-chlorophenyl-N-phenylcarbamate. a) 1M HClO$_4$, b) 5×10^{-6}M, c) 1×10^{-5}M, d) 5×10^{-5}M, e) 1×10^{-4}M, f) 5×10^{-4}M, g) 1×10^{-3} M.

terception of both the cathodic and anodic Tafel curves. The higher inhibition efficiency of these compounds may result from planar orientation of the adsorbed molecules on the
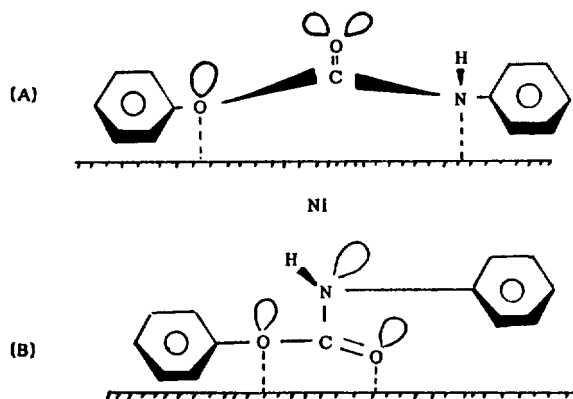
Figure 2. Schematic representation of the modes of adsorption of phenyl N-phenylcarbamate.
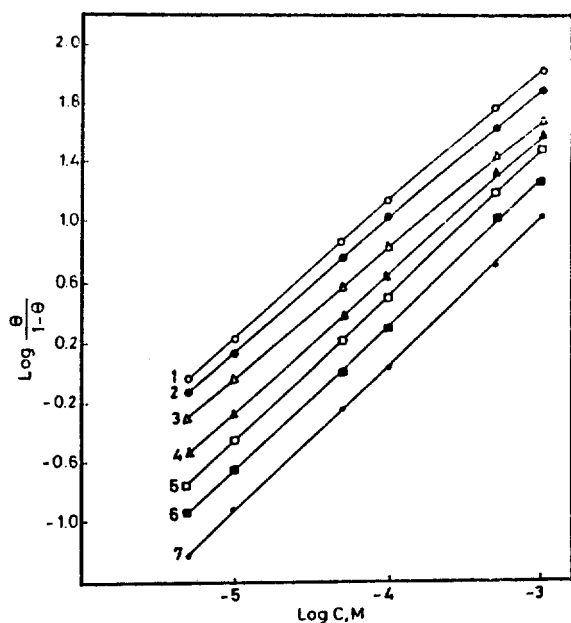

Figure 3. Adsorption isotherms for the seven mono-substituted phenyl N-phenylcarbamate.

Figure 4. Electrocapillary curves for 1M $HClO_4$ at 27°C showing the effect specific adsorption of 3(p-chlorophenyl N-phenylcarbamate) concentrations are (in M): a) 0, b) 5×10^{-6}, c) 1×10^{-5}, d) 1×10^{-4}, e) 1×10^{-3}.

nickel surface. The inhibition efficiencies vary widely due to the variable adsorbabilities of these compounds on the nickel surface.

Figure 2 shows that there are two possible modes of adsorption of inhibitors (A) and (B). Mode (A) covers a larger area of the metal surface than mode (B). Adsorption isotherms obtained from equation (1) are presented in Figure 3. These are Langmiur isotherms in which $\log \frac{\theta}{1-\theta}$ is linear in log concentration. Similar results were obtained by the authors[22,23] for the corrosion inhibition of copper in HNO_3 in the presence of substituted phenols and of aluminium in HCl in the presence of azo dyes.

The values of free energy of adsorption, ΔG_{ads} (Tables 1 and 2), were calculated using the following equations[24]:

$$\log C = \log \frac{\theta}{1-\theta} - \log A \qquad (2)$$

$$\log A = -1.74 - \frac{\Delta G_{ads}}{2.303RT} \qquad (3)$$

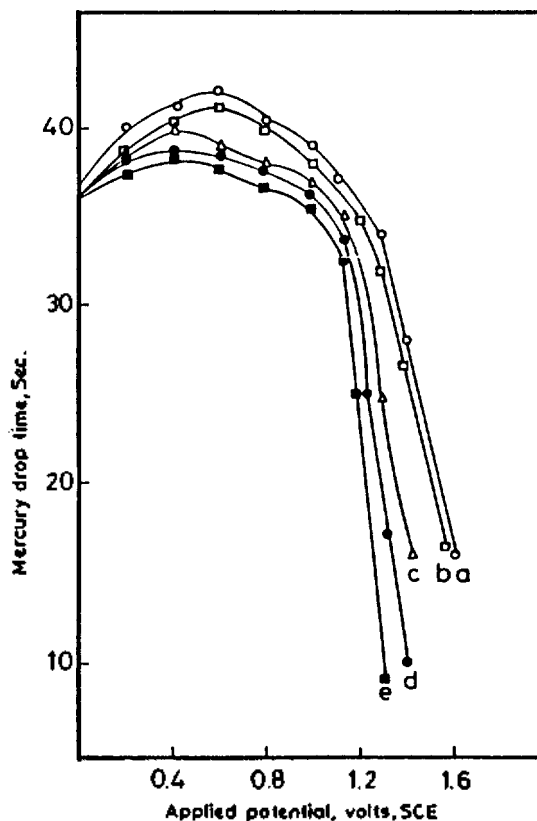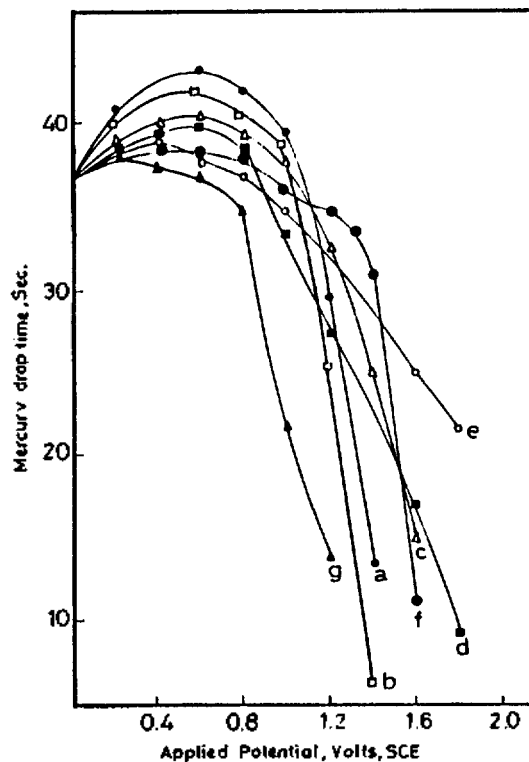The negative values of ΔG_{ads} indicate that the adsorption

Figure 5. Electrocapillary curves for 1M $HClO_4$ and $10^{-3}M$ inhibitors at 27°C. a) 1M $HClO_4$, b) 7, c) 6, d) 5, e) 3, f) 2, g) 1.

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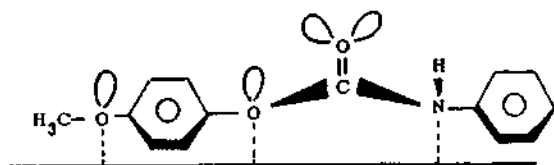*Bull. Korean Chem. Soc., Vol. 10, No. 6, 1989* 567

Figure 6. Schematic representation of the mode of adsorption of *p*-methoxyphenyl N-phenylcarbamate.

of the inhibitors on a nickel surface is a spontaneous process.

Figure 4 shows the electrocapillary curves for the adsorption of inhibitor 3 from 1M $HClO_4$ solution. The results show that the amount of inhibitor adsorbed increases with an increase in concentration.

Figure 5 shows that the inhibitor 1 is adsorbed almost strongly and inhibitor 7 is least one adsorbed. This may be attributed to the increased number of donor sites of inhibitor 1 compared to the other inhibitors tested. Inhibitor 7 has only two centers of adsorption (N atom of NH group and O atom of the phenoxy group) and there is no substituent in the *p*-position of the phenoxy group.

Structure–Inhibition Relationship. Polarization measurements indicate the following order in the inhibitive power for the studied compounds: 1>2>3>4>5>6>7. Inhibition efficiency depends on many factors including basicity, number of adsorption sites or functional groups, molecular size, mode of interaction and heat of reaction[25]. In the present case the N atom of the NH group and the oxygen atom of the phenoxy group are probable centers for cathodic and anodic adsorption.

The basicity of the N atom of the NH group and the oxygen atom of the phenoxy group are apparently constant due to unchanged structural environment. However, the basicity of these centers of adsorption may be affected by the polar character of substituents in the para and meta positions of the phenoxy group. The order of the effect of electron release is: H<*m*-CH$_3$<*m*-Cl<*p*-Cl<*p*-Br<*p*-CH$_3$<*p*-OCH$_3$.

This order is almost concordant with the observed order of inhibition efficiency (1>2>3>4>5>6>7), except compound 4 comes before 2 and 3. Compounds 2 and 3 give higher inhibition efficiency than compound 4, this may be due to their molecular size (Br>Cl>CH$_3$). Compound 1 has the highest inhibition efficiency. This may be due to the increased number of donor sites (Figure 6), or to the increase of the basicity of the donor sites due to the presence of a *p*-methoxy group.

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