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ROLE OF THE THIOCYANATE ION IN THE CORROSION INHIBITION OF ZINC IN PERCHLORIC ACID BY n-DECYLAMINE

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Summary

The effect of KSCN on the corrosion of electropolished zinc in 0.1 M $HClO_4$ and 0.1 M $HClO_4$ solution containing different concentrations of n-decylamine (nDA) has been investigated using weight loss and polarization methods. The inhibitor efficiency of nDA increased markedly in the presence of KSCN. pH and temperature affected the corrosion inhibition of zinc by nDA in acidic KSCN solution. The weight loss and polarization measurements gave consistent results. nDA in acidic KSCN solution acted mainly as a cathodic inhibitor, but with a smaller degree of anodic control. The increase in the inhibitor efficiency of nDA in the presence of KSCN is discussed from the viewpoint of the co-adsorption of nDA in cationic form and thiocyanate ions.

1. Introduction

The study of the corrosion inhibition of metals by amines has been the subject of many investigations. Amines function as corrosion inhibitors in aqueous solution by adsorption at the metal/solution interface [1 - 3]. The extent of adsorption of an inhibitor depends on many factors [4 - 6] : (a) the nature of the metal; (b) the surface condition; and (c) the mode of adsorption of the inhibitor. The adsorption theory of corrosion inhibition, postulating that adsorption is general over the entire surface, was first proposed by Hackerman [7 - 9]. The adsorption of n-decylamine (nDA) on solid electrodes has been reported [10, 11]. The type of interaction of the corrosion inhibitor on the metal surface has been evaluated from adsorption isotherms [12]. n-Decylamine has been used as a corrosion inhibitor for steel [13]. The corrosion inhibition of zinc in acid solution by nDA and the synergistic effect of nDA and halide ions have been studied extensively in this laboratory [14 - 16].

The effect of thiocyanate ion and nDA on the corrosion of zinc in acid solution was found to be different from the effect of halide ions and nDA. The present communication deals with the effect of the thiocyanate ion on the corrosion inhibition of zinc in perchloric acid solution by n-decylamine.

2. Experimental

The materials used for the experiment were $HClO_4$ (Rdl) nDA (Fluka AG) and KSCN (AR). The solutions were prepared using fresh triple-distilled water. Zinc (99.999%) was fixed in Tygon tubing and mechanically polished on 0000 emery paper, using ethanol as lubricant. The electropolishing of the zinc surface was carried out in 35% (volume) orthophosphoric acid in ethanol at a cell potential of 3.5 V for 8 min, using a stainless steel plate as cathode [14, 17]. Free dissolution (spontaneous dissolution) was carried out in a stirred solution of perchloric acid with and without various concentrations of nDA, KSCN, and mixtures of KSCN and nDA at 30 °C. At critical concentrations of addition agents, free dissolution was carried out at different temperatures (30 to 50 °C) and at different concentrations of $HClO_4$ solution.

The weight loss during free dissolution was determined by estimating the amount of zinc dissolved in solution using a colorimetric method [18].

The anodic and cathodic polarization of zinc was carried out galvanostatically with and without critical concentrations of addition agents. The detailed experimental procedure has been given elsewhere [15].

3. Results

The dissolution of zinc was carried out for various periods of immersion with and without addition agents. Linear variation of weight loss of zinc in

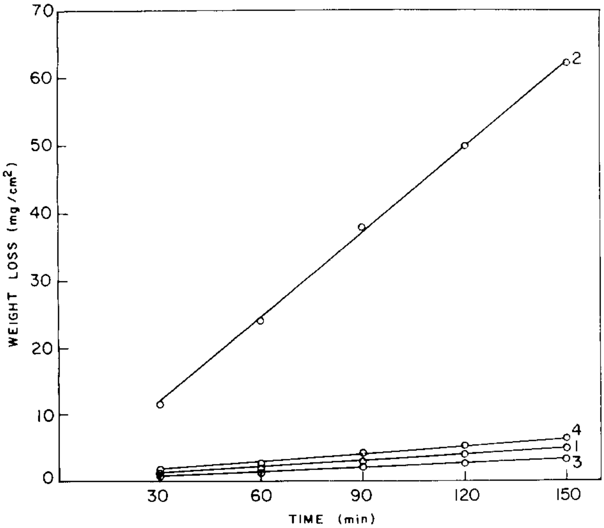

Fig. 1. Variation of weight loss with time at 30 °C during the corrosion of zinc in 0.1 M $HClO_4$ with: (1) no addition agents; (2) 0.01 M KSCN; (3) 5×10^{-3} M nDA; (4) 0.01 M KSCN + 5×10^{-3} M nDA.

$HClO_4$ solution with time (Fig. 1) was observed with and without addition agents, indicating steady rate of dissolution.

The weight loss of zinc in 0.1 M perchloric acid solution containing different concentrations of nDA was determined. Table 1 shows the corrosion rate at different concentrations of nDA. The pH of 0.1 M perchloric acid was not altered by the addition of nDA up to 10^{-2} M. The dissolution rate of zinc decreased with increase in nDA concentration. 10^{-2} M nDA decreased the corrosion of zinc from 2.16 to 1.27 mg cm^{-2} h^{-1}, indicating 41% corrosion inhibition. The corrosion potential shifted from −685 mV to −650 mV in the presence of 10^{-2} M nDA.

TABLE 1

Corrosion potential, weight loss and surface coverage at different concentrations of nDA in 0.1 M $HClO_4$

Molar concentration	Corrosion potential (mV)	Weight loss (mg $cm^{-2}h^{-1}$)	Surface coverage θ
0	−685	2.16	
10^{-3}	−680	1.92	0.11
2.5×10^{-3}	−680	1.71	0.21
5×10^{-3}	−670	1.50	0.30
7.5×10^{-3}	−660	1.35	0.38
10^{-2}	−650	1.27	0.41

Table 2 shows the effect of KSCN on the corrosion of zinc in 0.1 M $HClO_4$ solution. A marked increase in the corrosion rate was observed with the addition of KSCN. The corrosion rate increased from 2.16 to 24.2 mg cm^{-2} h^{-1} with the addition of 10^{-2} M KSCN to 0.1 M $HClO_4$ solution. The corrosion potential shifted from −685 mV to −760 mV with the addition of 10^{-2} M KSCN. Increasing the concentration of KSCN to 10^{-1} M, the corrosion rate and corrosion potential changed to 30.3 mg cm^{-2} h^{-1} and −780 mV, respectively. The smell of H_2S and the corrosion product ZnS on the surface were also noticed during the dissolution in perchloric acid containing KSCN.

The experiments were carried out with different concentrations of nDA in $HClO_4$ solution containing 10^{-2} M KSCN. A significant decrease in the corrosion rate was observed with the addition of nDA. In the presence of 10^{-2} M nDA, the corrosion rate decreased from 24.2 mg cm^{-2} h^{-1} to 2.1 mg cm^{-2} h^{-1}, corresponding to 91.3% inhibition. The corrosion potential also shifted significantly with the addition of nDA to the solution of $HClO_4$ containing KSCN.

Table 3 shows the corrosion rate and corrosion potential at various concentrations of nDA in $HClO_4$ solution containing KSCN.

The effect of KSCN on the corrosion of zinc in perchloric acid containing nDA was studied. The corrosion inhibition of zinc by 5×10^{-3} M nDA

TABLE 2

Effect pf KSCN concentration on corrosion rate and corrosion potential of zinc in 0.1 M $HClO_4$ at 30 °C

Molar concentration	Corrosion rate ($mg\ cm^{-2}\ h^{-1}$)	Corrosion potential (mV)
0	2.16	−685
10^{-5}	2.18	−685
10^{-4}	3.12	−690
5×10^{-4}	7.92	−700
10^{-3}	12.40	−715
5×10^{-3}	19.40	−740
10^{-2}	24.20	−760
2.5×10^{-2}	26.20	−765
5×10^{-2}	27.50	−770
7.5×10^{-2}	29.50	−775
10^{-1}	30.30	−780

TABLE 3

Effect of nDA concentration on dissolution rate, corrosion potential and surface coverage of zinc in 0.1 M $HClO_4$ + 10^{-2} M KSCN

Molar concentration	Corrosion rate ($mg\ cm^{-2}\ h^{-1}$)	Corrosion potential (mV)	Surface coverage θ
0	24.2	−760	
10^{-4}	20.0	−750	0.17
2×10^{-4}	18.2	−740	0.26
5×10^{-4}	15.0	−720	0.38
10^{-3}	9.30	−705	0.62
2.5×10^{-3}	6.25	−695	0.74
5×10^{-3}	2.60	−690	0.89
7.5×10^{-3}	2.40	−685	0.90
10^{-2}	2.10	−685	0.903

was found to be only 30%. The inhibition increased with increase in concentration of KSCN. An inhibition of 89% was noticed in the presence of 5×10^{-3} M nDA, when the concentration of KSCN was 5×10^{-3} M.

The corrosion potential in 0.1 M $HClO_4$ changed by 15 mV in the presence of 5×10^{-3} M nDA. The change in corrosion potential with the same concentration of nDA, in $HClO_4$ containing KSCN, is given in Table 4.

Free dissolution was carried out at different temperatures in the following baths: (a) 0.1 M $HClO_4$, (b) 0.1 M $HClO_4$ + 0.01 M KSCN, (c) 0.1 M $HClO_4$ + 5×10^{-3} M nDA and (d) 0.1 M $HClO_4$ + 0.01 M KSCN + 5×10^{-3} M nDA. Increase in temperature increased the corrosion rate in baths (a) and (b), whereas in solutions (c) and (d), the corrosion rate decreased. Thus, the inhibitor efficiency of 5×10^{-3} M nDA increased with increase in temper-

TABLE 4

Variation of surface coverage of zinc surface by 5×10^{-3} M nDA at different concentrations of KSCN in $HClO_4$ solution at 30 °C

Bath solution	Corrosion potential (mV)	Dissolution rate (mg cm^{-2} h^{-1})	Surface coverage θ
0.1 M $HClO_4$	−685	2.16	0.30
0.1 M $HClO_4$ + 5×10^{-3} M nDA	−675	1.60	
0.1 M $HClO_4$ + 10^{-4} M KSCN	−690	3.12	0.50
0.1 M $HClO_4$ + 10^{-4} M KSCN + 5×10^{-3} M nDA	−675	1.55	
0.1 M $HClO_4$ + 5×10^{-4} M KSCN	−700	7.92	0.79
0.1 M $HClO_4$ + 5×10^{-4} M KSCN + 5×10^{-3} M nDA	−680	1.60	
0.1 M $HClO_4$ + 10^{-3} M KSCN	−715	12.40	0.85
0.1 M $HClO_4$ + 10^{-3} M KSCN + 5×10^{-3} M nDA	−685	1.90	
0.1 M $HClO_4$ + 5×10^{-3} M KSCN	−740	19.40	0.89
0.1 M $HClO_4$ + 5×10^{-3} M KSCN + 5×10^{-3} M nDA	−690	2.10	
0.1 M $HClO_4$ + 10^{-2} M KSCN	−760	24.20	0.89
0.1 M $HClO_4$ + 10^{-2} M KSCN + 5×10^{-3} M nDA	−690	2.60	

ature, *i.e.* 0.30 at 30 °C to 0.50 at 50 °C in 0.1 M $HClO_4$. In 0.1 M $HClO_4$ containing 5×10^{-3} M KSCN the inhibitor efficiency of 5×10^{-3} M nDA increased from 0.89 at 30 °C to 0.93 at 50 °C. Table 5 shows the inhibitor efficiency of 5×10^{-3} M nDA at different temperatures.

TABLE 5

Effect of temperature on corrosion inhibition of zinc by 5×10^{-3} M nDA in $HClO_4$ with and without KSCN

Temperature (°C)	Percentage protection	
	In 0.1 M $HClO_4$	In 0.1 M $HClO_4$ + 0.01 M KSCN
30	30.5	89.0
40	42.0	91.0
50	50.0	93.0

The addition of 5×10^{-3} M nDA did not alter the pH of $HClO_4$ under study. The inhibitor efficiency of nDA was also determined at different pH values by free dissolution experiments. Table 6 indicates the increase in the corrosion inhibition of zinc by nDA with increase in pH.

TABLE 6

Effect of perchloric acid concentration on corrosion inhibition of zinc by 5×10^{-3} M nDA

Concentration of $HClO_4$ (M)	pH	Percentage protection	
		In $HClO_4$	In $HClO_4$ + 0.01 M KSCN
0.05	1.30	39	91.5
0.10	1.00	30	89.0
0.25	0.60	23	84.0
0.50	0.30	19	75.0

To understand the mechanism of corrosion inhibition, anodic and cathodic polarization studies were made galvanostatically in 0.1 M $HClO_4$ with and without addition agents at 30 °C (Figs. 2 and 3). At a particular current density, the polarization decreased with the addition of KSCN, and the polarization increased with the addition of nDA to 0.1 M $HClO_4$. The increase in polarization with the addition of nDA was more in 0.1 M $HClO_4$ + 0.01 M KSCN than in 0.1 M $HClO_4$. The anodic Tafel slope of 30 ± 5 mVs was not changed by the addition of either addition agent, KSCN or nDA. The cathodic Tafel slope of 120 ± 10 mV was also unaffected by the addition of KSCN. However, the slope increased to 290 mV with the addition of 5×10^{-3} M nDA to both 0.1 M $HClO_4$ and 0.1 M $HClO_4$ containing KSCN.

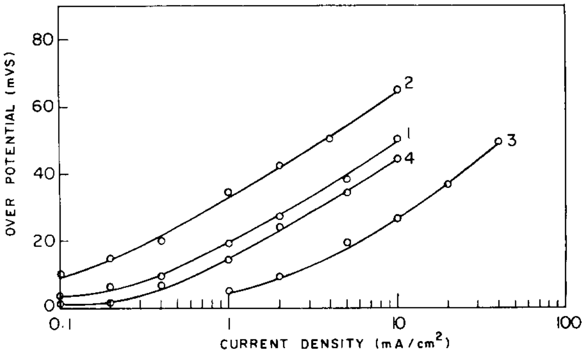

Fig. 2. Galvanostatic anodic polarization of zinc at 30 °C in 0.1 M $HClO_4$ containing (1) no addition agents; (2) 5×10^{-3} M nDA; (3) 0.01 M KSCN; (4) 0.01 M KSCN + 5×10^{-3} M nDA.

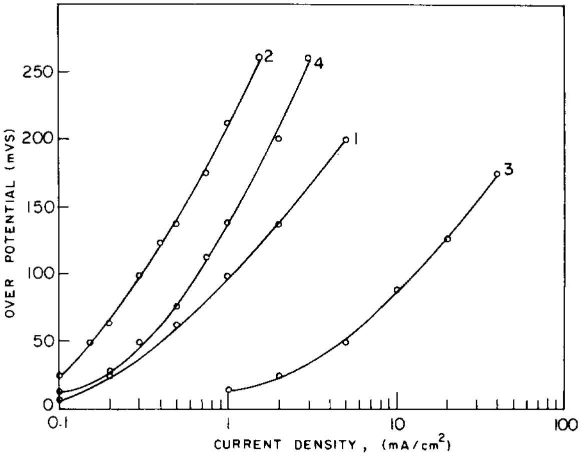

Fig. 3. Galvanostatic cathodic polarization of zinc at 30 °C in 0.1 M $HClO_4$ containing (1) no addition agents; (2) 5×10^{-3} M nDA; (3) 0.01 M KSCN; (4) 0.01 M KSCN + 5×10^{-3} M nDA.

The corrosion current densities were determined by extrapolating anodic and cathodic Tafel lines to free corrosion potential values. The inhibitor efficiency calculated from the weight loss and the Tafel extrapolation methods are given in Table 7. Consistency in the value of inhibitor efficiency was noted.

4. Discussion

The corrosion rate of zinc in 0.1 M $HClO_4$ decreased with the addition of nDA. A marked increase in the corrosion rate was observed with the addition of KSCN to 0.1 M $HClO_4$. The addition of nDA to 0.1 M $HClO_4$

TABLE 7

Comparison of surface coverage of nDA (5×10^{-3} M) with and without KSCN in $HClO_4$ by weight loss and an electrochemical method

Bath solution	Corrosion current ($mA\,cm^{-2}$)	Surface coverage	
		Electrochemical method	Weight loss method
0.1 M $HClO_4$	0.15	0.33	0.30
0.1 M $HClO_4$ + 5×10^{-3} M nDA	0.10		
0.1 M $HClO_4$ + 0.01 M KSCN	2.0	0.90	0.89
0.1 M $HClO_4$ + 0.01 M KSCN + + 5×10^{-3} M nDA	0.20		

containing KSCN decreased the corrosion rate of zinc drastically. The inhibitor efficiency of nDA was a function of the concentration of nDA and KSCN. Decrease in the corrosion rate was associated with a shift in corrosion potential towards the more noble direction.

The corrosion inhibition of zinc by nDA was affected by the temperature and pH of the solution. Increase in pH and temperature increased the inhibitor efficiency of nDA.

The acid corrosion of zinc is electrochemical in nature, consisting of anodic dissolution of zinc with the second electron removal as the rate-determining step [19] and cathodic hydrogen evolution with the combination of adsorbed hydrogen atom on the surface as the slowest step [20]. The specific adsorption of inhibitor on the surface is the main factor that determines the corrosion inhibition of metals [21]. Halide ions are known to adsorb on the metal surface and the extent of adsorption depends on their polarizability [22].

The inhibiting action of nDA in 0.1 M $HClO_4$ and the synergistic effect of halide ions during the corrosion inhibition of zinc by nDA have been extensively discussed from the viewpoint of co-adsorption of halide ions and nDA [14, 16]. The free energy of adsorption of nDA under different conditions is also reported.

The net reaction during the acid corrosion of zinc is

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \qquad (1)$$

KSCN in $HClO_4$ may give sulphide ions (S^{2-}), which results in the following parallel reactions along with reaction (1)

$$Zn + S^{2-} \rightarrow ZnS + 2e \qquad (2)$$

$$ZnS + 2H^+ \rightarrow H_2S + Zn^{2+} \qquad (3)$$

Hence, one would expect acceleration of the corrosion of zinc in $HClO_4$ solution in the presence of KSCN.

Zinc in acid solution has a negative potential on the ϕ scale [23]. The protonated nDA molecules in acid solution tend to adsorb on the cathodic sites of the zinc surface, which brings about the inhibition of cathodic evolution of hydrogen. This is in accordance with increase in the cathodic Tafel slope in the presence of nDA (Fig. 3). The constant anodic Tafel slope in $HClO_4$ solution with and without nDA indicates that the mechanism of anodic dissolution of zinc in $HClO_4$ solution was not changed by nDA (Fig. 2). However, the displacement of anodic overpotential towards the more noble direction may be due to the blocking of anodic sites on the zinc surface by nDA.

Zinc in $HClO_4$ solution containing KSCN attains a more negative corrosion potential than in $HClO_4$. This favours a better electrostatic condition for nDA cations to adsorb on the electrode surface. Hence, one would expect an increase in the inhibitor efficiency of nDA in $HClO_4$ solution containing KSCN (Table 1).

The decrease in the corrosion inhibition of zinc by nDA with decrease in pH may be explained by the fact that the solubility of nDA increases with decrease in pH. This decreases the surface concentration of nDA at the electrode/solution interface, and hence one would expect a decrease in corrosion inhibition with decreasing pH of the solution. The increase in corrosion inhibition with increase in temperature indicates a strong electrostatic interaction of chemisorbed nDA cations on the zinc surface.

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