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Phenyl Semicarbazide Derivatives as Corrosion Inhibitors for Aluminium in Hydrochloric Acid Solution

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Summary. Measurements of the corrosion rate of aluminium in $2N$ HCl at 27°C with and without addition of phenyl semicarbazide derivatives ($10^{-3}-10^{-5}$ mol/l) were performed. The adsorption of these compounds was elucidated. Results show that phenyl semicarbazide derivatives are adsorbed on the aluminium surface according to the Frumkin isotherm. From the adsorption isotherm some thermodynamic data for the adsorption process ($\Delta G^{\circ}_{ads.}$ and f) are calculated and discussed.

Keywords. Corrosion; Phenyl semicarbazide.

Phenylsemicarbazide als Korrosionsinhibitoren für Aluminium in salzsauren Lösungen

Zusammenfassung. Es wurden Messungen der Korrosionsgeschwindigkeit von Aluminium in $2N$ HCl bei 27 °C mit und ohne Zusatz von Phenylsemicarbaziden ($10^{-3}-10^{-5}$ mol/l) durchgeführt. Es wurde die Adsorption dieser Verbindungen untersucht, wobei sich zeigte, daß die Adsorption der Phenylsemicarbazidderivate der Frumkin-Isotherme gehorcht. Aus der Isotherme wurden einige thermodynamische Parameter des Adsorptionsprozesses ($\Delta G^{\circ}_{ads.}, f$) berechnet.

Introduction

Despite the extensive use of inhibitors to decrease corrosion, little is known of their function because of the complexity of the process. Understanding of the inhibitive action during corrosion requires a knowledge of the adsorption of inhibitor at the electrode-solution interface [1]. Adsorption isotherms of the inhibitors for the corrosion process have been discussed [2–4]. The Frumkin [5] isotherm has the formula

$$BC = \frac{\theta}{1-\theta}\exp(-f\theta), \qquad (1)$$

where C is the concentration of the adsorbed substance in the bulk of the solution and θ is the degree of coverage of the metal surface by the inhibitor. B is the modified equilibrium constant of the adsorption process, which is related to the standard free energy of adsorption according to the following equation:

$$B = \exp\left(-\frac{\Delta G^{\circ}_{ads.}}{RT}\right)\frac{1}{55.5}. \qquad (2)$$

In Eq. (1) f is a constant depending on intermolecular interactions in the adsorption layer and on the heterogeneity of the surface. This parameter can either be positive or negative, but cannot have arbitrary large positive values.

Mann [6, 7] studied the adsorption of various aliphatic amines on iron oxide, Bockris [8] investigated the adsorption of *n*-dodecylamine on iron oxide, Simialowska and Wieczorek studied the adsorption of straight chain aliphatic amines, acids and alcohols on steel [9].

The present investigation examines the adsorption of phenyl semicarbazide derivatives on an aluminium surface from hydrochloric acid solution.

Experimental

Commercial-grade aluminium (composition %: Si 0.15, Fe 0.19, Mn 0.005, Mg 0.1, Cu 0.02, Al remainder) was used. All chemicals used were of AR grade except the inhibitors which were chemically pure substances. The solutions were made from distilled water. The weight-loss experiments were carried out on specimens in the form of sheets (2 cm × 2 cm). The surface was mechanically polished on different grades of emery paper and then degreased in a degreasing mixture (15 g Na_2CO_3 + 15 g Na_3PO_4 per liter).

Anodic polarization experiments were carried out under unstirred conditions with a fine luggin capillary to avoid ohmic polarization. Galvanostatic condition was maintained using a constant current (WP-704 AX). Aluminium was taken in the form of cylindrical rod with a surface area of 0.37 cm^2. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively. The potentials were recorded using an Orion digital ionalyzer (Model 701 A). For each experiment a new specimen was used.

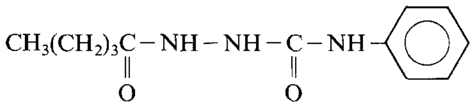
The degree of coverage of the investigated surface by the adsorbed molecules was calculated from the equation

$$\theta = 1 - \frac{u}{u_0}, \tag{3}$$

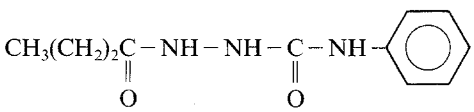
where u_0 and u are the dissolution rates in absence and in presence of the investigated compounds, respectively. Since the slope of the Tafel line (parameter b in the equation $E = a + b \log i$), corresponding to the transition from pure hydrochloric acid to solutions containing the examined compounds, is constant (60 ± 5 mV/decade), Eq. (3) can be used to calculate the degree of coverage θ, assuming that the adsorbed molecules of the chemical substance mechanically screen the coated part of the electrode surface and therefore protect it from the action of the corrosive medium. But the degree of surface coverage calculated from this equation is inaccurate. This is due to the fact that the adsorption on the electrode depends not only on the adsorptive power of the organic compound and the character of the metal but also on the electrode potential and on the potential drop in the diffuse part of the double layer. The adsorbed molecules can change the charge of the electrode and consequently also its potential, and as a result inaccurate values for θ calculated from Eq. (3) are obtained. For accurate θ values calculated from Eq. (3) some additional conditions must be fulfilled: changes in electrode potential caused by adsorption of the inhibitor, the heterogenity of the metal surface, and the choice of concentration of the electrolyte, which made the potential drop in the diffuse part of the double layer; all these parameters must be small.

The investigated inhibitors were:

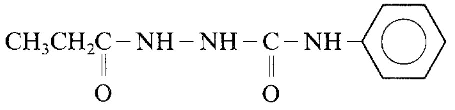
I: 1-Valeroyl-4-phenyl-3-semicarbazide



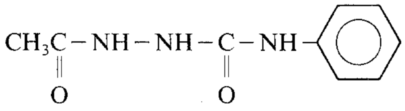
II: 1-Butroyl-4-phenyl-3-semicarbazide



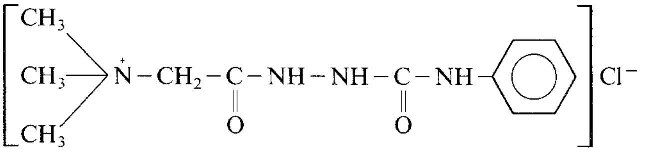
III: 1-Propionoyl-4-phenyl-3-semicarbazide



IV: 1-Acetyl-4-phenyl-3-semicarbazide



V: 1-Acetyltrimethylammonium chloride-4-phenyl-3-semicarbazide



Results and Discussion

Aluminium was dissolved in HCl solution containing various concentrations ($10^{-6} - 10^{-3}\,M$) of phenyl semicarbazide derivatives at 27°C and the dissolution rates were calculated. These compounds were found to have a significant effect on the dissolution rate. The dissolution rate decreases gradually with the increase in concentration of phenyl semicarbazide derivatives. Fig. 1 shows the variation of dissolution rate and inhibitor efficiency (P) with concentration of inhibitor **I**. The anodic overpotential of aluminium in HCl solution at various concentrations of inhibitor **I** is shown in Fig. 2. An increase in the concentration of inhibitor shifted the polarization curves towards more positive potentials. An anodic Tafel slope of $60 \pm 5\,\mathrm{mV}$ was obtained with and without phenyl semicarbazide derivatives.

The degree of coverage (θ) of aluminium surface by different concentrations of phenyl semicarbazide derivatives was calculated using Eq. (3). Fig. 3 shows the plot of $\theta = f(\log C)$ which has the characteristic S-shape. In the analysis the isotherms having the S-shape in the θ-log C system of coordinates, Frumkin's approach was considered.

Using B and f values obtained from Eqs. (1) and (2) it was possible to calculate some of the thermodynamical quantities characterizing the adsorption process.

The experimental data are collected in Table 1. They indicate that inhibitor **V** has the lowest standard free energy of adsorption. It is also the least effective as metal protecting agent. The other inhibitors, which are more effective corrosion inhibitors, have also higher standard free energy of adsorption values. However, this relationship is only qualitative and cannot be expressed by a general equation.

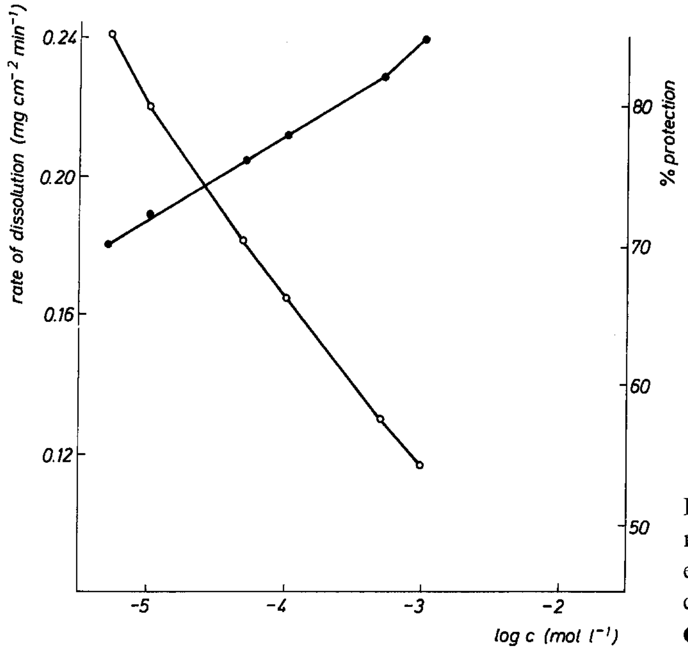


Fig. 1. Variation of dissolution rate and % inhibition with 1-valeroyl-4-phenyl-3-semicarbazide concentration (○ dissolution rate, ● % protection)

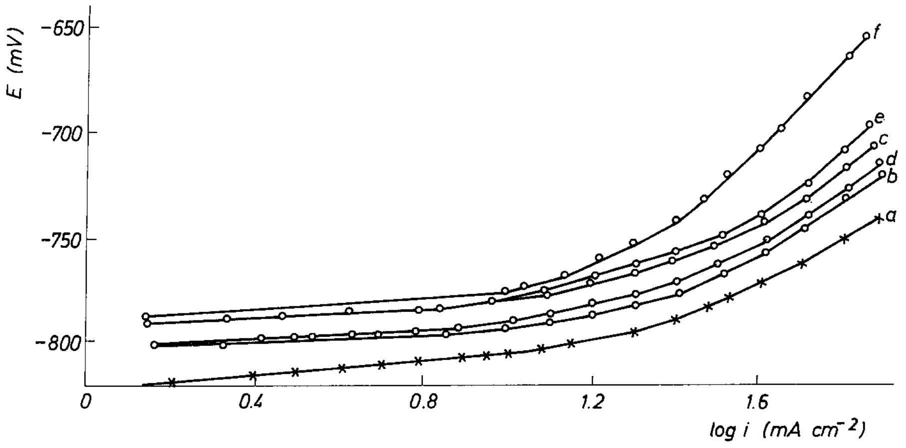


Fig. 2. Effect of 1-valeroyl-4-phenyl-3-semicarbazide on the anodic polarization of aluminium in 2*N* HCl; (*a*) blank; (*b*) $1 \cdot 10^{-5}$mol/l; (*c*) $5 \cdot 10^{-5}$mol/l; (*d*) $1 \cdot 10^{-4}$mol/l; (*e*) $5 \cdot 10^{-4}$mol/l; (*f*) $1 \cdot 10^{-3}$mol/l

This can be seen in Fig. 4, showing the relation between the protective effectiveness (P) and the standard free energy of adsorption ($\Delta G^{\circ}_{ads.}$).

The standard free energies of adsorption values ($\Delta G^{\circ}_{ads.}$) of the phenyl semicarbazide derivatives are within the limits of 5–10 kcal/mol which have been observed for the majority of organic inhibitors of various types in aqueous media [10].

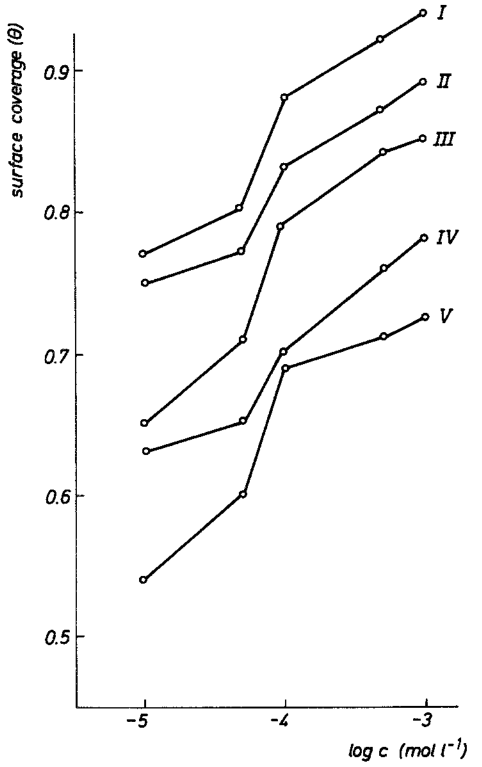


Fig. 3. The dependence of the degree of coverage of aluminium surface in $2N$ HCl at 27°C on the concentration of adsorbing substances

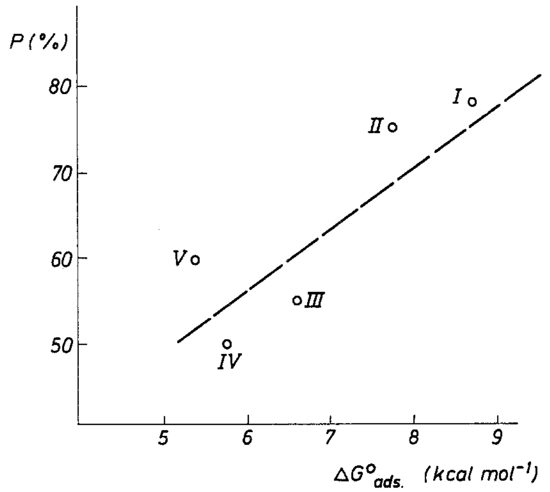


Fig. 4. The dependence of the protective effectiveness of the examined compounds on their standard free energy of adsorption ($\Delta G^{\circ}_{ads.}$); inhibitor concentration $5 \cdot 10^{-5}$ mol/l

The ability of the inhibitors to adsorb on metallic surfaces is in the order: **V** < **IV** < **III** < **II** < **I**. This is in confirmity with the decrease in the chain length of these compounds. Inhibitor **V** has the lowest inhibitive power. This may be attributed to the positive charge on the N-atom which decreases the electron density on the molecule. The results show that the inhibitive power increases with the increase in the chain length of the compounds used. This agrees with the results

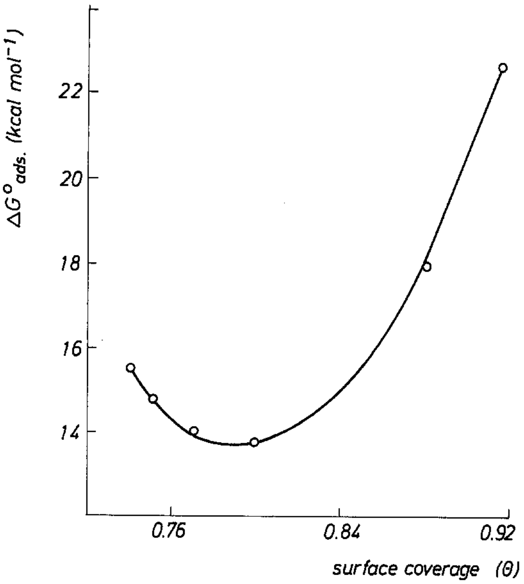


Fig. 5. $\Delta G^{\circ}_{ads.}$ for inhibitor *I* on aluminium as a function of surface

Table 1. Thermodynamical data calculated from experimental isotherms of adsorption of phenyl semicarbazide derivatives in HCl at 27°C

Inhibitor	f	Adsorption equilibrium constant (log K)[a]	B mol^{-1} K^{-1}	$-\Delta G^{\circ}_{ads.}$ kcal/mol
I	0.81	6.30	$4.2 \cdot 10^4$	8.70
II	2.55	5.64	$9.4 \cdot 10^3$	7.80
III	5.11	4.78	$1.3 \cdot 10^3$	6.60
IV	7.03	4.20	$3.4 \cdot 10^2$	5.80

[a] $\log K = \Delta G^{\circ}_{ads.}/2.303\,RT$

reported before [11]. The positive values of f (Table 1) indicate that adsorption of these compounds is accompanied by mutual attraction of the molecules.

The variation of $\Delta G^{\circ}_{ads.}$ with θ (Fig. 5) indicates the change in the mechanism of inhibitor action with inhibitor **I** concentration. On the basis of earlier works [12–14] and the observed results, the three models of adsorption proposed before [15] can be applied.

The negative values $\Delta G^{\circ}_{ads.}$ indicate that the adsorption of inhibitors on the aluminium surface is a spontaneous process. Also the increase in the negative values of $\Delta G^{\circ}_{ads.}$ with θ indicates that there is a lateral interaction between adsorbed inhibitor molecules on the surface [8].

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