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Efficiency of Some Phenylthiosemicarbazide Derivatives in Retarding the Dissolution of Al in NaOH Solution

A. S. Fouda* and **A. A. Elasmy**

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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Five derivatives of phenylthiosemicarbazide have been prepared and treated as inhibitors for the corrosion of aluminium in 2 *M* sodium hydroxide. All the five substances afford 98.5 to 75% protection to aluminium in sodium hydroxide. 1(-Methoxybenzoyl)-4-phenyl-3-thiosemicarbazide being the most efficient inhibitor. Thermometric and weight loss methods indicate that the inhibition is principally governed by the adsorption of these compounds on the surface of the aluminium metal and the adsorbability of inhibitors is dependent on the basicity of the oxygen and sulphur sites involved.

(Keywords: Corrosion; Inhibitor)

Die Effizienz einiger Phenylthiosemicarbazid-Derivate in der Verzögerung der Auflösung von Al *in* NaOH-*Lösung*

Es wurden fünf Derivate von Phenylthiosemicarbazid hergestellt und als Inhibitoren für die Korrosion von Aluminium in 2 *M* NaOH eingesetzt. Die Substanzen ergaben 98.5 bis 75% Schutz für Aluminium in NaOH. Dabei war 1-(Methoxybenzoyl)-4-phenyl-3-thiosemicarbazid der effizienteste Inhibitor. Thermometrische und Gewichtsverlustmethoden zeigten, daß die Inhibition prinzipiell von der Adsorption dieser Verbindungen auf der Metalloberfläche gesteuert wird, wobei die Adsorbierbarkeit der Inhibitoren von der Basizität der teilnehmenden Sauerstoff- und Schwefelfunktionen abhängt.

Introduction

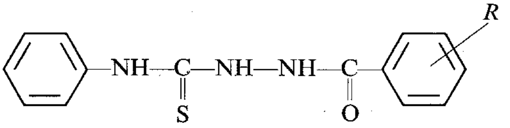
Sulphur-containing organic compounds are potential inhibitors of corrosion [1]. Recent studies [2–8] have shown that carbonyl compounds inhibit the corrosion of aluminium. The inhibition is attributed to [3, 4] adsorption of the organic compounds on the aluminium surface through the carbonyl group. The charge density on both the C=O and C=S affects the inhibition efficiency. In the present investigation, an attempt has been made to prepare some phenylthiosemicarbazide derivatives and to investigate the inhibitive power of these derivatives towards aluminium corrosion in sodium hydroxide solution.

Experimental

Preparation of the inhibitors

All inhibitors except 1-Benzoyl-4-phenyl-3-thiosemicarbazide (which was prepared as before [9]), were prepared by adding an equimolecular amount of phenylisothiocyanate with the corresponding acid hydrazides (*p*-methoxybenzoylhydrazide, *p*-methylbenzoylhydrazide, *o*-chlorobenzoylhydrazide and *p*-nitrobenzoylhydrazide) in absolute ethanol. The mixtures were refluxed for 0.5 h, the crystals which formed on heating were filtered off, washed, recrystallized from absolute ethanol and finally dried in a vacuum desiccator over anhydrous chloride.

Compound	m.p. °C	% Calculated		% Found	
		C	H	C	H
1: 1-(*p*-methoxybenzoyl)-4-phenyl-3-thiosemicarbazide	178	59.78	5.01	60.00	5.00
2: 1-(*p*-methylbenzoyl)-4-phenyl-3-thiosemicarbazide	156–166	63.14	5.30	63.40	5.12
3: 1-(*o*-chlorobenzoyl)-4-phenyl-3-thiosemicarbazide	148	54.99	3.95	55.05	4.07
4: 1-Benzoyl-4-phenyl-3-thiosemicarbazide	162	61.97	4.83	62.00	4.53
5: 1-(*p*-nitrobenzoyl)-4-phenyl-3-thiosemicarbazide	176	53.15	3.82	53.10	3.90



	R
1	*p*-OCH_3
2	*p*-CH_3
3	*o*-Cl
4	H
5	*p*-NO_2

2 *M* NaOH solutions were used in all experiments. All test pieces measuring 1 × 10 × 100 mm were used for thermometric, while 1 × 20 × 20 mm test pieces were used for the weight loss method. The alkali (2 *M* NaOH), degreasing mixture and additive solutions were prepared as previously described [10]. The stock

solutions of the inhibitors were prepared from absolute alcohol and it remained homogeneous by dilution and throughout the reaction time.

The procedures and apparatus employed in thermometric and weight loss measurements were practically the same as reported in earlier communications [11]. In thermometric measurements the reaction number, *RN*, is defined as $(T_m - T_i)/t\,^{\circ}\mathrm{C\,min}^{-1}$ where T_m and T_i are the maximum and initial temperatures, respectively, and t is the time from the start up to the attainment of maximum temperatures. The efficiency of a given inhibitor was evaluated as the percentage reduction in reaction number, viz.:

$$\%\ \text{Reduction in } RN = \frac{(RN)_{\text{free}} - (RN)_{\text{inh}}}{(RN)_{\text{free}}} \cdot 100$$

$(RN)_{\text{free}}$ and $(RN)_{\text{inh.}}$ are the reaction numbers of aluminium dissolution in free alkali and in presence of the given inhibitor.

Results and Discussion

Temperature-time curves of aluminium in 2 *M* NaOH were followed in the absence and in the presence of the studied inhibitors. When the concentration of the added inhibitor increases, the thermometric curves are influenced as shown in Fig. 1. As shown in the Fig. 1 the curves for additive containing systems fall below that of the free alkali. This indicates that the additives behave as inhibitors over the concentration range studied. Curves having the same character are obtained with other tested inhibitors. The curves of Fig. 2 relate the reaction number *RN* of all the additives to the logarithm of their concentrations.

The reaction number-log *C* curves consist of an initial descending portion along which *RN* decreases with increasing inhibitor concentration up to a certain limit. Above this limit the rate of decrease in *RN* values becomes smaller as can be gathered from the smaller value of the slope. However, as the concentration of the additive increases further, the values of *RN* decrease linearly with concentration and then become more or less constant. This behaviour is explainable on the basis of a two-step adsorption process [12]. The plots of $\log \Delta t$ vs. concentration of the additives (Fig. 3) are in confirmity with this explanation. First, the curves consist each of an initial linear portion which passes to a region of constancy which is an indication of the completion of a monolayer of the adsorbate, second, there is again a second rise in $\log \Delta t$ before the values attain constancy which indicates the formation of the second layer.

The data in Table 1 showing the per cent reduction in *RN* for the various additives at the same concentration, indicate that the efficiency of corrosion inhibition as calculated from the reduction in *RN* varies with both the type and the concentration of the additive used.

Reference to Fig. 1 indicates that both T_m and t values are affected, the former being lowered and the latter increased. According to [10] weakly

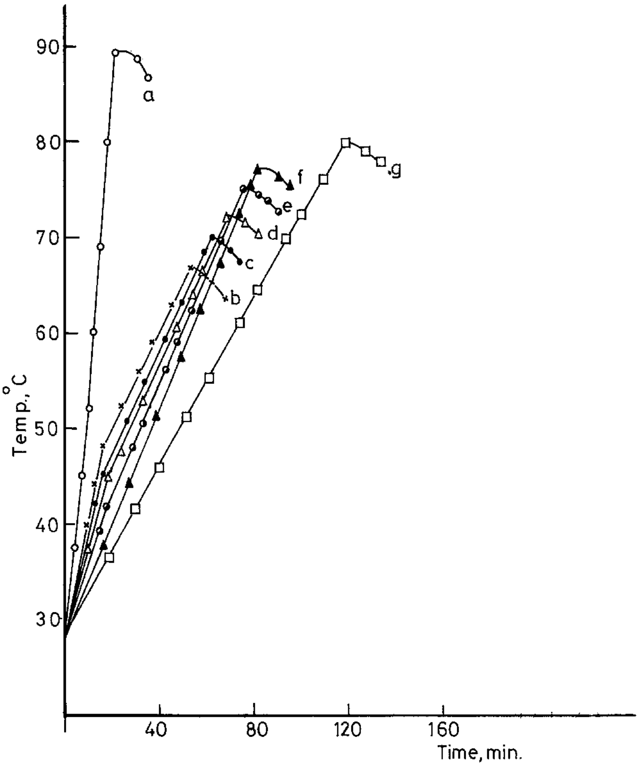


Fig. 1. Temperature-time curves obtained in absence and in presence of varying concentrations of **3**: *a* free alkali; *b* $1 \cdot 10^{-6} M$; *c* $5 \cdot 10^{-6} M$; *d* $10^{-5} M$; *e* $5 \cdot 10^{-5} M$; f) $10^{-4} M$; g) $5 \cdot 10^{-4} M$

Table 1. *Efficiency of corrosion inhibition as determined by percentage reduction in reaction number (RN) in* 2 *M* NaOH

Conc. of the additive in M/L	% Reduction in *RN*				
	1	**2**	**3**	**4**	**5**
$5 \cdot 10^{-4}$	98.5	86.6	85.1	83.8	75.0
$1 \cdot 10^{-4}$	97.1	84.5	79.6	65.7	63.9
$5 \cdot 10^{-5}$	95.2	83.9	79.2	61.1	47.6
$1 \cdot 10^{-5}$	94.9	83.3	78.2	59.3	45.6
$5 \cdot 10^{-6}$	94.7	82.2	76.9	57.0	41.1
$1 \cdot 10^{-6}$	90.1	77.4	70.1	52.0	34.6

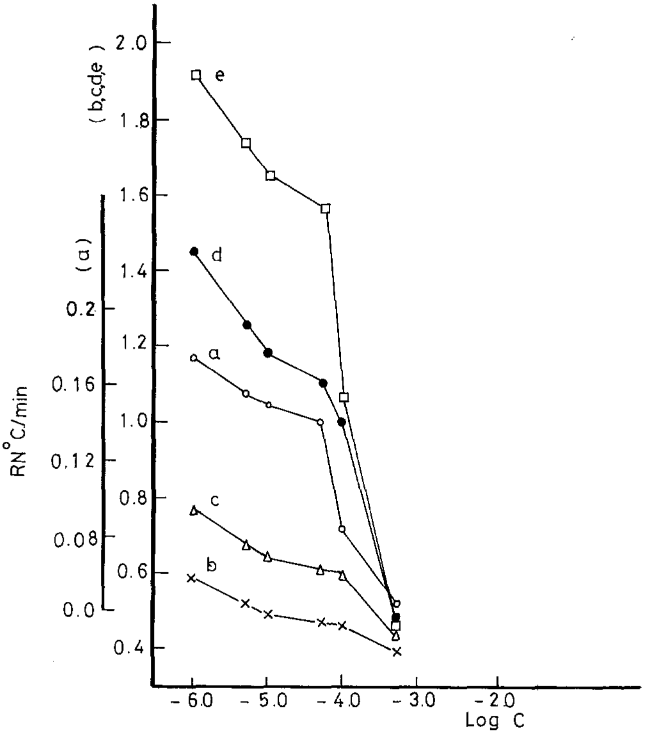


Fig. 2. Variation of reaction number *RN* with the logarithm of concentration of all additives used: *a* p-OCH_3; *b* p-CH_3; *c* o-Cl; *d* p-NH_2; *e* p-NO_2

adsorbed inhibitors reduce *RN* by increasing t without affecting T_m, since a longer time would be taken for the displacement of the adsorbed inhibitor, before subsequent normal reaction occurs between the exposed metal surface and the alkali. In contrast, for strongly adsorbed inhibitors no displacement of adsorbed inhibitor is likely to take place and accordingly both T_m and t values are affected, i.e. T_m being lowered and t increased.

From the above considerations, all the inhibitors studied fall in the category of strongly adsorbed inhibitors.

The loss in the weight of aluminium strips in 2 *M* NaOH in the absence and in the presence of different concentrations of the various inhibitors was determined. The weight loss of 1-(p-methoxybenzoyl)-4-phenyl-3-thiosemicarbazide (**1**) is plotted in Fig. 4 as a function of time. The inhibition efficiences of the additives after 60 minutes are included in

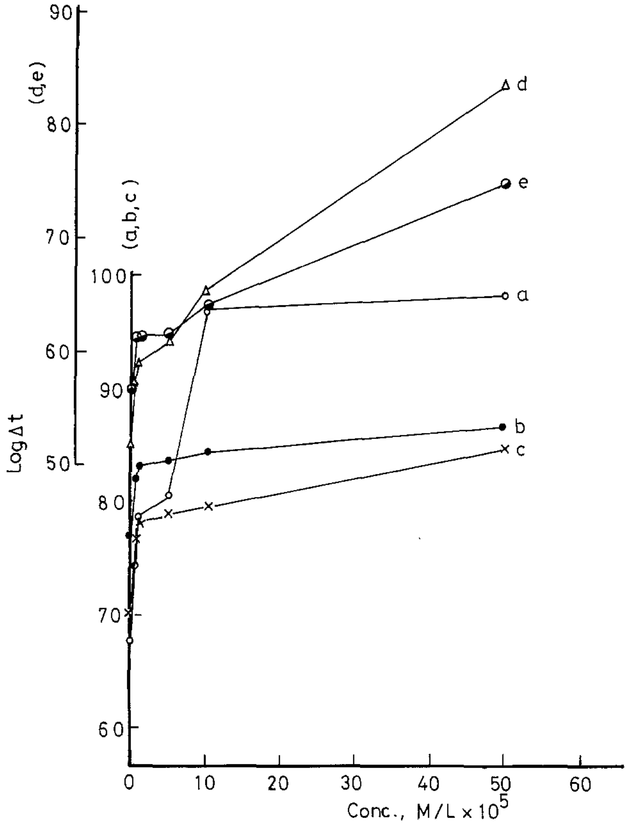


Fig. 3. % Reduction in *RN*-concentration curves for all additives used: *a* *p*-OCH_3; *b* *p*-CH_3; *c* *o*-Cl; *d* *p*-H; *e* *p*-NO_2

Table 2. In this Table the inhibitors used are arranged in the order of decreasing inhibition. The same order is obtained from both the experimental methods employed.

In conclusion, the adsorption of the organic compounds investigated on the metal surface would take place through a functional groups, essentially C=S and C=O, and would depend essentially on its charge density.

The adsorbability of the studied compounds decrease in the order **1** > **2** > **3** > **4** > **5** as shown in Table 3. This is due to the comparable decrease in the basicity of C=O and C=S due to the increased electronegative character of the atoms or groups attached to the *p*- or *o*-positions to the phenyl ring of the hydrazide residue.

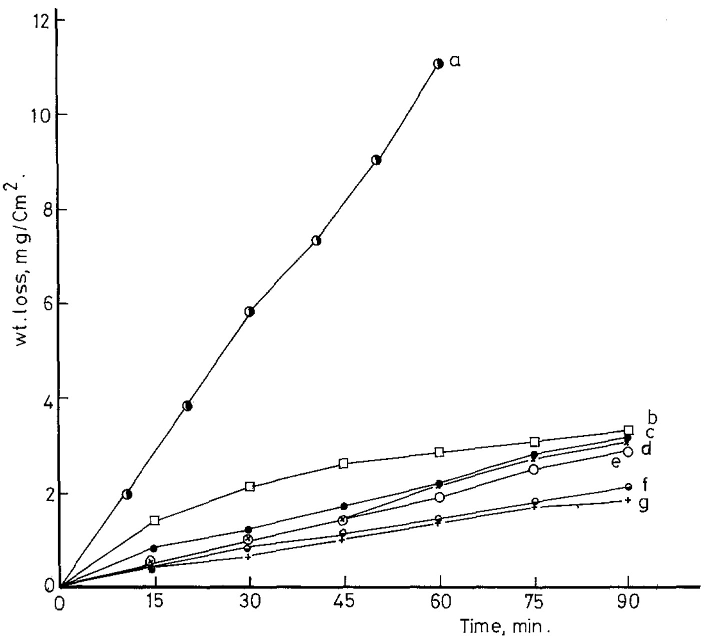


Fig. 4. Weight loss-time curves for **1**: *a* free NaOH; *b* $1 \cdot 10^{-6} M$; *c* $5 \cdot 10^{-6} M$; *d* $1 \cdot 10^{-5} M$; *e* $5 \cdot 10^{-5} M$; *f* $1 \cdot 10^{-4} M$; *g* $5 \cdot 10^{-4} M$

Table 2. *Effect of inhibitor concentration on the percentage inhibition in* NaOH *solution after 60 minutes*

Conc. of the additive, in *M/L*	% Inhibition				
	1	**2**	**3**	**4**	**5**
$5 \cdot 10^{-4}$	88.3	80.0	77.4	73.9	20.5
$1 \cdot 10^{-4}$	87.3	79.1	67.8	66.3	17.5
$5 \cdot 10^{-5}$	82.3	75.2	63.5	60.6	8.5
$1 \cdot 10^{-5}$	81.1	70.0	57.0	56.4	8.3
$5 \cdot 10^{-6}$	79.9	68.3	47.8	45.3	7.9
$1 \cdot 10^{-6}$	74.8	65.4	45.3	43.2	7.4

1 is the most efficient inhibitor. This is due to the higher electron donation character of —OCH_3 compared to the other substituents. For compounds **2**–**4** adsorption takes place through C=O and C=S but the basicity of the substituents increases in the order *p*-CH_3 > *o*-Cl > *p*-H, so we observe that the inhibition efficiency of these compounds increase in

Table 3. *Comparison between efficiency of corrosion as determined by thermometric and weight loss techniques, at a concentration of* $5 \cdot 10^{-4}$ *M*

Inhibitor added	% Reduction in *RN*	% Inhibition*
5	75.0	20.5
4	83.8	73.9
3	85.1	77.4
2	86.6	80.0
1	98.5	88.3

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* At 60 min from the beginning of dissolution

the order **2** > **3** > **4**. Compound **5** is one with the lowest corrosion inhibition property. This can be attributed to *p*-NO_2 which is an electron attracting group; on the other hand, it lowers the charge density on C=O and C=S, and hence the inhibition efficiency is decreased.

Fouda [13], *Kapali* [14], *Neanaa* [15], and other investigators reported that the inhibition efficiency in sodium hydroxide solution is very low, but in the present investigation we obtained higher inhibition efficiency in the same medium (Tables 1, 2), expect for compound **5**. This can be attributed to a) the higher molecular size of the tested inhibitors b) the complete solubility of the inhibitors in sodium hydroxide solution and c) the aluminium complexes which may be formed with these compounds are soluble in alkaline solution.

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