

## Regularities of the residual protective effect of the *o*-hydroxyazomethine reaction series toward aluminum corrosion in 1 M H<sub>2</sub>SO<sub>4</sub>

V. P. Grigor'ev,<sup>1\*</sup> S. P. Shpan'ko,<sup>1</sup> E. V. Plekhanova,<sup>1</sup> A. S. Burlov<sup>2</sup>  
and Yu. M. Plastun<sup>1</sup>

<sup>1</sup> Southern Federal University, ul. Zorge 7, Rostov-on-Don, 344090 Russian Federation

\*E-mail: [valentgrig@mail.ru](mailto:valentgrig@mail.ru)

<sup>2</sup> Research Institute of Physical and Organic Chemistry at Southern Federal University, pr. Stachki 94/3, 344104 Rostov-on-Don, Russian Federation

### Abstract

The regularities of changes in the residual protective effect of *o*-hydroxyazomethine derivatives on the acid corrosion of Al have been studied. The duration of the residual protective effect ( $\tau$ ) is a function of the polarity of substituents in *o*-hydroxyazomethine molecules, inverse temperature of the solution, and the additive concentration in the pre-adsorption solution. The identified regularities of the effect of these factors on  $\tau$  is interpreted in terms of the Linear Free Energy Relationship approach. The changes in the near-electrode concentration of a desorbed inhibitor as a function of time and solution temperature are discussed. It is noted that the effects of various factors on the regularities of changes in the residual protective effect of *o*-hydroxyazomethine derivatives toward Al and Fe corrosion are similar.

**Key words:** corrosion, inhibitor, residual protective effect, LFE concept, near-electrode concentration, effective activation energy.

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### Introduction

The residual protective effect (RPE) of acid corrosion inhibitors toward iron, a transition metal, has been studied [1, 2]. This paper reports a comparative study of the RPE for a non-transition metal, in particular aluminum.

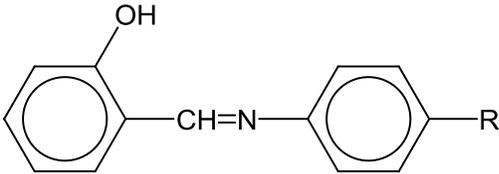
### Objects of the study and experimental procedure

The corrosion of AD-1 aluminum [GOST (USSR state standard) 1946-50] was studied in 1 M H<sub>2</sub>SO<sub>4</sub> solution. Inhibitors (or their mixtures) were pre-adsorbed on Al for 24 h from 1 M H<sub>2</sub>SO<sub>4</sub> solutions containing the corresponding inhibitor(s).

Derivatives belonging to the *o*-hydroxyazomethine reaction series (RS) with electron-donating and electron-withdrawing substituents R [3] were used as the inhibitors. Mixtures for pre-adsorption solutions were composed of these compounds. Each of the mixtures

contained  $n$  compounds of this RS ( $n = 1-4, 6$ ). The polarity of R was estimated by Hammett  $\sigma$ -constants, Table 1.

**Table 1.** *o*-Hydroxyazomethine reaction series, substituents R, and their Hammett  $\sigma$ -constants

Formula	R	$\sigma$	R designation
	H	0	1
	CH <sub>3</sub>	-0.17	2
	OC <sub>2</sub> H <sub>5</sub>	-0.25	3
	OCH <sub>3</sub>	-0.268	4
	OH	-0.37	5
	N(CH <sub>3</sub> ) <sub>2</sub>	-0.6	6
	Cl	+0.227	7
	Br	+0.232	8
	COOC <sub>2</sub> H <sub>5</sub>	+0.522	9
	COOH	+0.728	10

The integral polarity of substituents in the molecules of inhibitor mixtures in pre-adsorption solutions at a total inhibitor concentration of  $C = 10^{-2}$  mol/l was calculated by the formula  $\sum_{i=1}^n N_i \sigma_i$  where  $N_i$  is the molar fraction of compound  $i$ ,  $\sigma_i$  is the polar constant for substituent  $R_i$ , and  $n$  is the number of compounds of this RS in the mixture [4]. The technique for the preparation of pre-adsorption solutions was reported previously [4, 5].

Prepared aluminum electrodes were weighed and transferred to the corresponding pre-adsorption solutions. After exposure for 24 h, the electrodes were dried with filtering paper and immersed in 1 M H<sub>2</sub>SO<sub>4</sub> solutions ( $t = 0$ ). After each subsequent time period  $t$ , the next three electrodes were retrieved and weighed to estimate the RPE parameter.

The RPE value was estimated by two characteristics:

$K_t$  – the RPE coefficient after time  $t$  from the start of corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> solution (without an inhibitor) – the reference solution:

$$K_t = \frac{\Delta m_0}{\Delta m_i},$$

where  $\Delta m_0$  is the mass loss of the sample over time  $t$  from the instant of its immersion in the reference solution;  $\Delta m_i$  is the same value for an electrode pretreated with an inhibitor or inhibitor mixture;

$\tau$  – the RPE duration calculated from the plots of  $K_t$  versus  $t$  at  $K_t = 1$ ,  $t = \tau$ .

The  $\Delta m$  values were determined by the weight loss method.

The dependence of  $K_t$  on the following parameters was studied: polarity  $\sigma$  of substituents R in molecules of the RS; the reference solution temperature; the concentration and number of inhibitors in the pre-adsorption solutions.

### Measurement results and discussion

All experiments, irrespective of the number of components in the pre-adsorption solutions, demonstrated a linear  $K_t - t$  plot described by equation (1), Fig. 1:

$$K_t = a - bt, \quad (1)$$

where  $a$  and  $b$  are constants.

The  $K_t = f(t)$  plots were obtained for the following mixtures:  $n = 2$  (7, 10), 2 (2, 6), 3 (1, 8, 10), 4 (1, 2, 4, 6), and 6 (1, 2, 3, 4, 5, 6). The numbers in parentheses correspond to the compound designations in Table 1. The plots below are provided for one mixture only. The plots for the other mixture compositions and temperatures are not presented since they look similarly.

Based on these plots, the  $\tau$  value was determined at  $K_t = 1$ . It linearly depends on the polarity of substituents in this RS ( $n = 1$ ) and on the integral polarity of substituents in the compound mixture at a constant total volume concentration of all  $n$  components

$\sum_{i=1}^n C_i = 10^{-2}$  mol/l, Fig. 2:

$$\tau = \text{const}_1 + \text{const}_2 \sum_{i=1}^n N_i \sigma_i \quad (2)$$

The plots of  $\tau$  versus concentration  $C$  of an individual inhibitor in pre-adsorption solutions (or their mixtures) at constant temperature  $T$  of the reference solution are shown in Fig. 3.

$$\tau = \text{const}_3 + \text{const}_4 \lg C \quad (T = \text{const}). \quad (3)$$

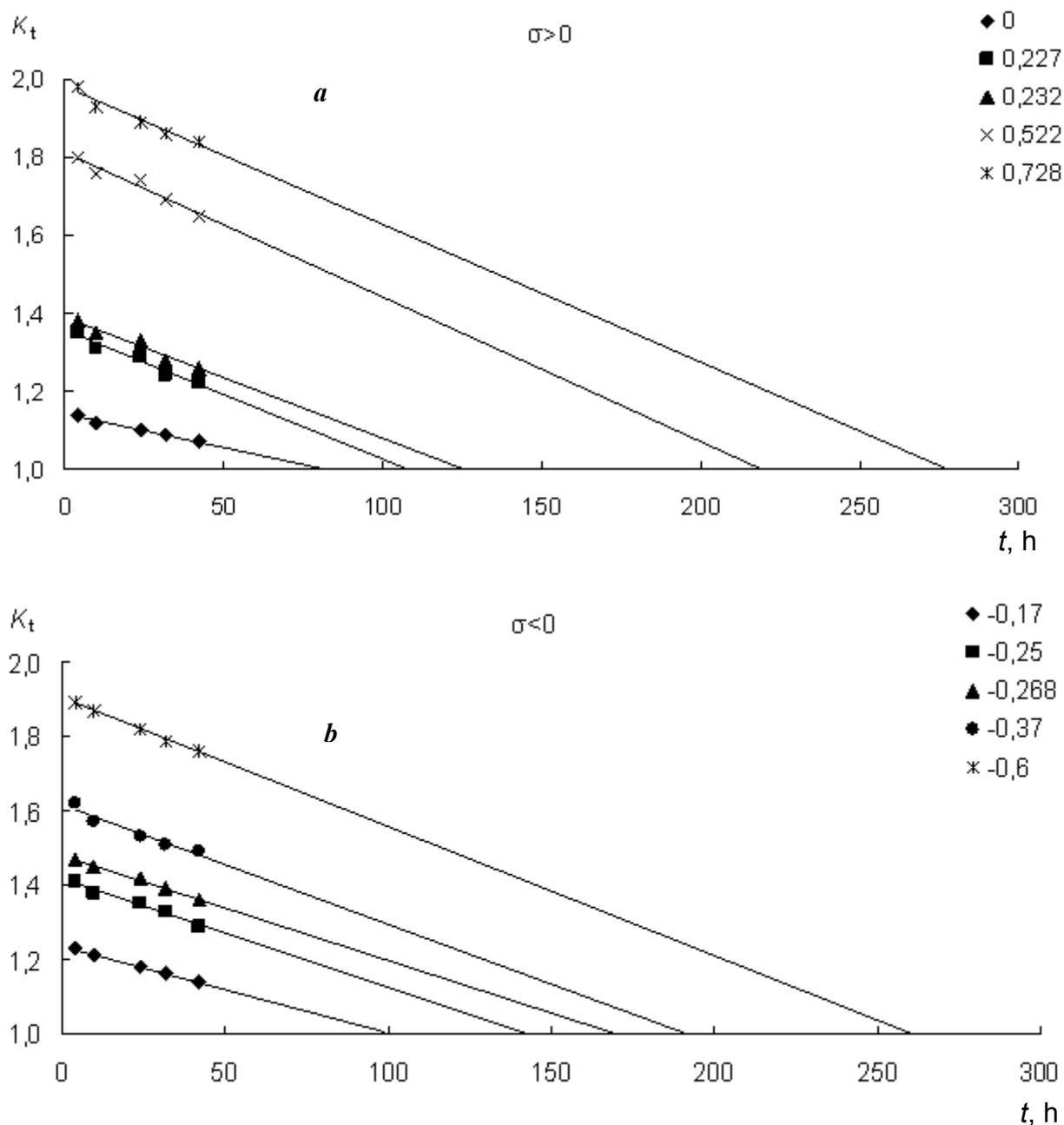
The plot of  $\tau$  versus  $T$  at constant concentration  $C$  under the conditions studied is described by equation (4), Fig. 4.

$$\tau = \text{const}_5 + \text{const}_6 1/T \quad (4)$$

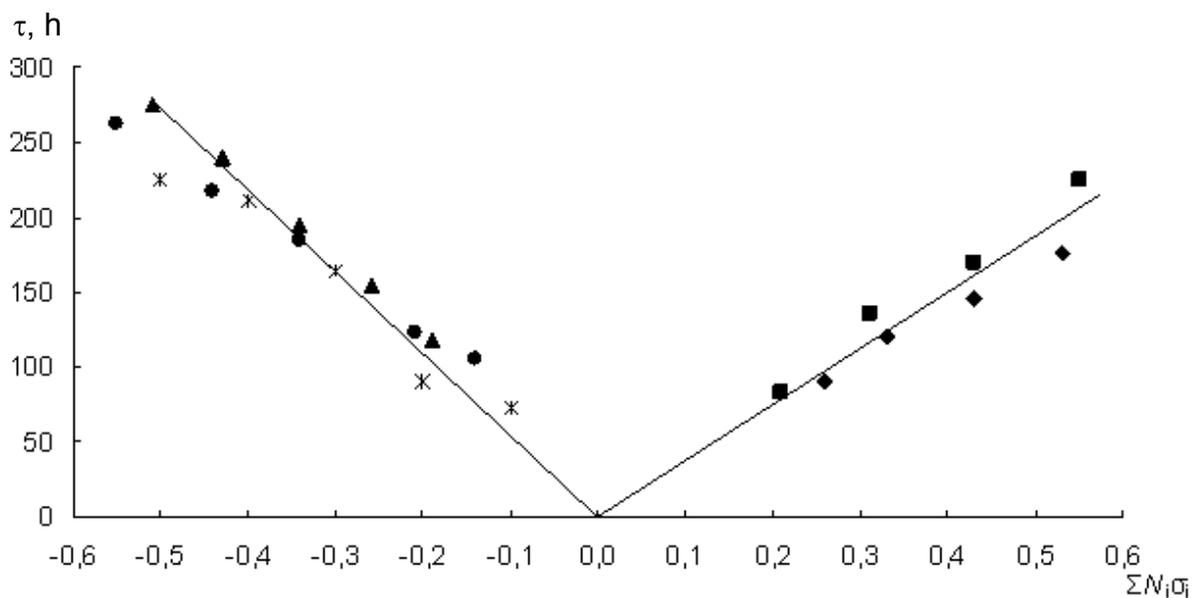
Relationships (1–4) were previously established for iron electrode in the presence of compounds of the same RS in pre-adsorption solutions and mathematically interpreted in [1].

Thus, this study allows us to conclude that the previously observed character of  $\tau$  plots for this RS on external conditions ( $\sigma$ ,  $T$ ,  $C$ ,  $\sum N_i \sigma_i$ ) is similar for Fe and Al electrodes and does not depend on whether a metal belongs to the transition or non-transition group.

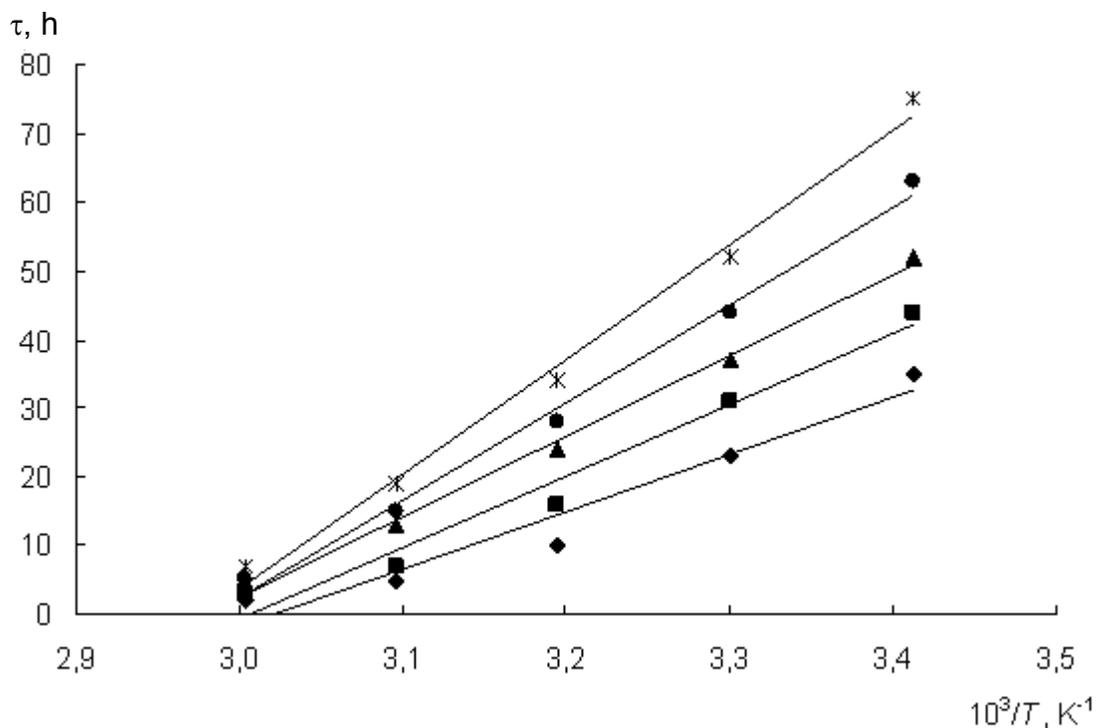
Furthermore, the previously presented method for the calculation of partial polarities of substituents [4] applied to mixtures of compounds of this RS based on LFE principle [5]



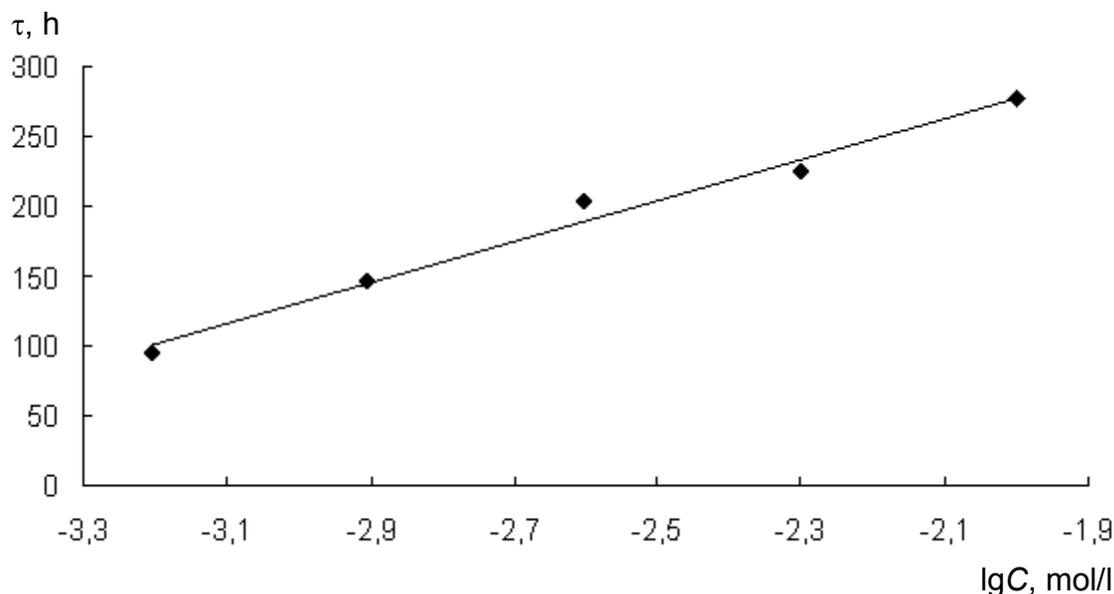
**Fig. 1.** Dependence of the residual protective effect coefficient during Al corrosion in 1 M  $H_2SO_4$  on time at 20°C after electrode pretreatment with a solution of *o*-hydroxyazomethine derivatives with substituents of different polarity: *a* –  $\sigma > 0$ ; *b* –  $\sigma < 0$ .



**Fig. 2.** Dependence of the residual protective effect duration  $\tau$  of individual *o*-hydroxyazomethine derivatives ( $n = 1$ ) and their mixtures ( $n > 1$ ) on the sum of partial polarities of substituents at 20°C. Number of components in the mixture,  $n$ :  $\times$  – 2 (2, 6);  $\blacklozenge$  – 2 (7, 10);  $\blacksquare$  – 3 (1, 8, 10);  $\blacktriangle$  – 4 (1, 2, 4, 6); \* – 6 (1, 2, 3, 4, 5, 6).



**Fig. 3.** Dependence of the residual protective effect duration  $\tau$  of *o*-hydroxyazomethine derivatives on inverse absolute temperature (the shapes of the points match the compounds in Fig. 2).



**Fig. 4.** Dependence of the residual protective effect duration  $\tau$  for the *o*-hydroxyazomethine derivative ( $R = \text{COOH}$ ) on concentration at  $20^\circ\text{C}$ .

proved to be valid not only for steady-state corrosion conditions where the inhibitor concentration at the electrode surface remains constant throughout the entire experiment but also under non-steady-state conditions, where an inhibitor was desorbed from the electrode surface and its concentration near the electrode surface changed in time.

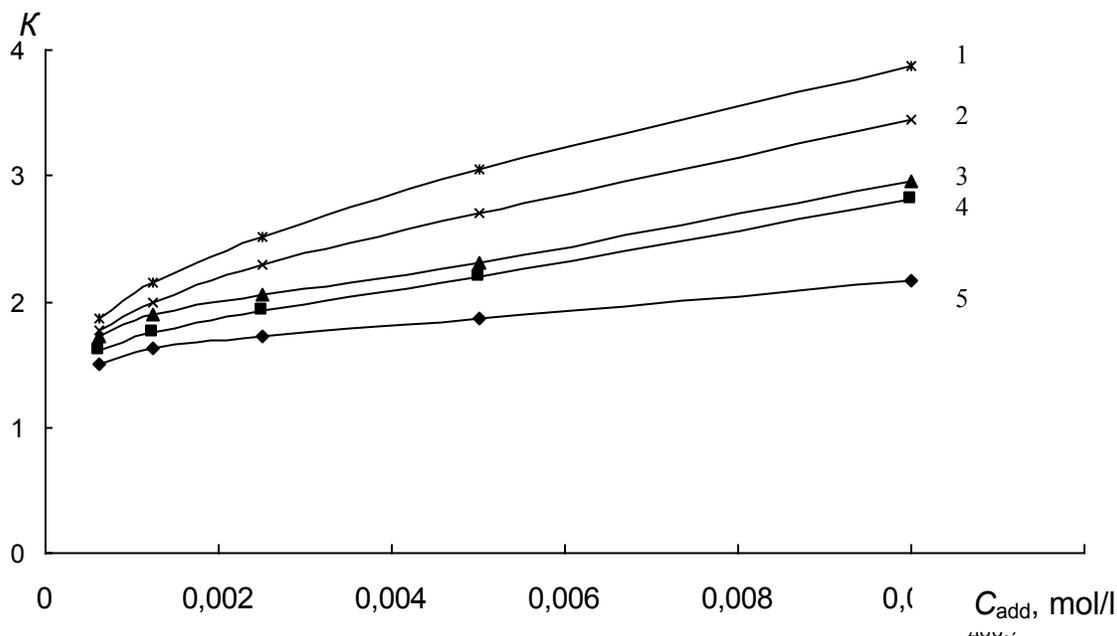
It is of interest to consider the change in the concentration  $C_s$  of the desorbed inhibitor with time and the related effective activation energies of the corrosion process,  $W_s$ . Obviously,  $C_s$  and  $W_s$  should depend on the inhibitor concentration in the pre-adsorption solution.

The subsequent discussion of experimental data is based on the assumption that the plot of corrosion inhibition coefficient  $K$  on the inhibitor concentration is the same both under steady-state corrosion conditions and in the case of desorption characterized by the residual protective effect  $K_t$ , *i.e.*,  $K_t = f(C)$ . In this case, based on the experimental plot  $K = f(C)$  for steady-state conditions and given the known  $K_t$  values for different  $t$ , it is possible to determine the corresponding  $C_s$  concentrations under RPE conditions and hence to find various electrochemical characteristics under desorption conditions as functions of concentration  $C_s$  for various points of time  $t$  from the start of surfactant desorption to the reference solution.

With this in mind, we first determined, under steady-state conditions, the relationships of  $K$  vs.  $C$  for aluminum corrosion in the presence of an *o*-hydroxyazomethine with substituent  $R = \text{COOH}$  in 1 M  $\text{H}_2\text{SO}_4$  solution in the temperature range  $20\text{--}60^\circ\text{C}$ , Fig. 5.

Based on these data, we plotted the relationships  $\lg j = f(1/T)$  that are linear, see Fig. 6. From these plots, we determined the effective corrosion activation energies  $W$  of aluminum

under steady-state conditions at various solution concentrations of the additive with  $R = \text{COOH}$ , Fig. 7.



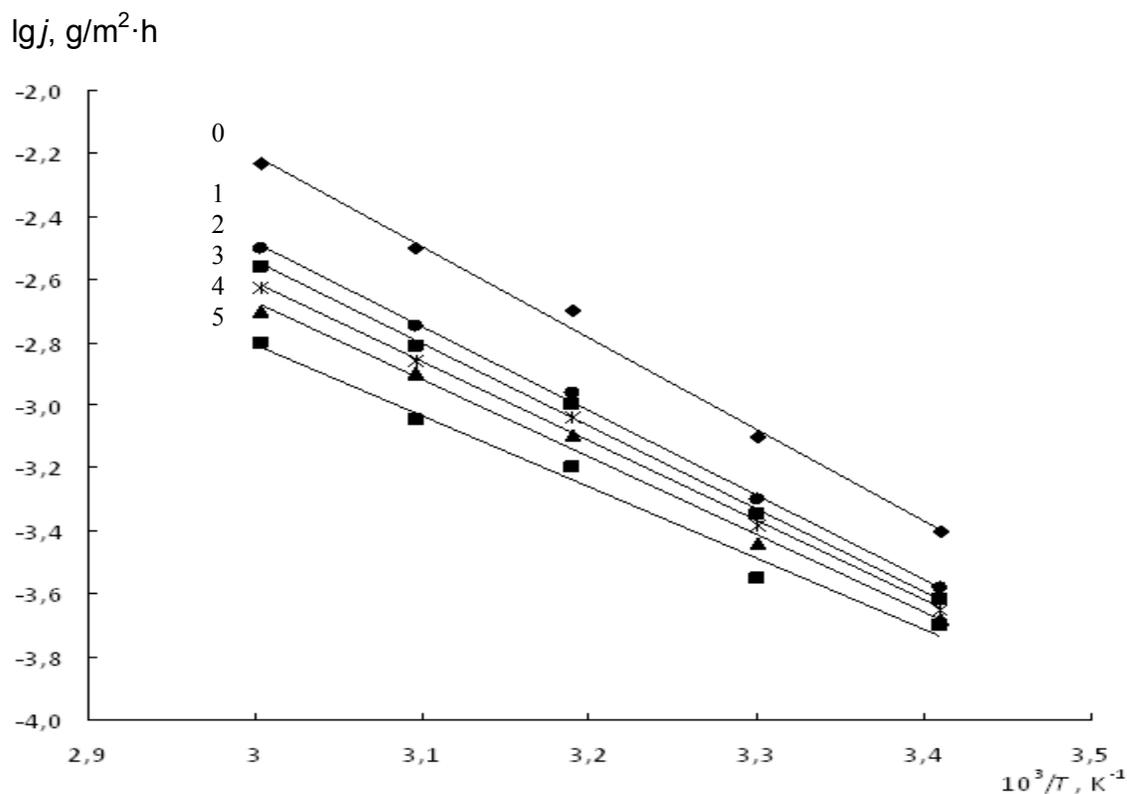
**Fig. 5.** Dependence of the corrosion inhibition coefficient for Al in 1 M  $\text{H}_2\text{SO}_4$  on the concentration of the *o*-hydroxyazomethine derivative ( $R = \text{COOH}$ ) at temperatures,  $^{\circ}\text{C}$ : 1 – 20; 2 – 30; 3 – 40; 4 – 50; 5 – 60.

The  $W$  values determined suggest that Al corrosion under steady-state conditions ( $C \neq f(t)$ ) occurs under activation control. Furthermore, the  $W$  value increases linearly with an increase in  $\lg C$  of the additive. This kind of  $W = f(C)$  relationship is quite common for acid corrosion of metals in inhibited media [6]. Similar measurements carried out for *o*-hydroxyazomethine derivatives with electron-donating substituents at  $C = 10^{-2}$  mol/l demonstrated a linear increase in  $W$  with an increase in  $\sigma$  values for the corresponding  $K$ , Fig. 8. The latter agrees with the previously established effect of  $\sigma$  on  $W$  [6], which additionally confirms the applicability of the Linear Free Energy (LFE) principle under the conditions studied.

By comparing the relationships  $K_t = f(C)$  for solutions containing an additive with  $R = \text{COOH}$  (Fig. 5) with the straight lines  $K_t = f(t)$  for the same  $t$ , Fig. 1, but for Al electrodes pretreated with the same inhibitor and immersed in 1 M  $\text{H}_2\text{SO}_4$ , we find the relationships  $C_s = f(t)$ , *i.e.*, the plots of the concentration of the inhibitor additive at the electrode surface as a function of time due to its desorption starting from the time of immersion of the inhibitor-treated electrode ( $t = 0$ ) into 1 M  $\text{H}_2\text{SO}_4$  reference solution, Fig. 9.

The resulting relationships  $C_s = f(t)$  reflect the considerable effect of the reference solution temperature on the rate of inhibitor desorption from the aluminum electrode surface.

The major part of desorption occurs during the starting period of time since immersion of inhibitor-treated electrodes into the reference solution. The higher the

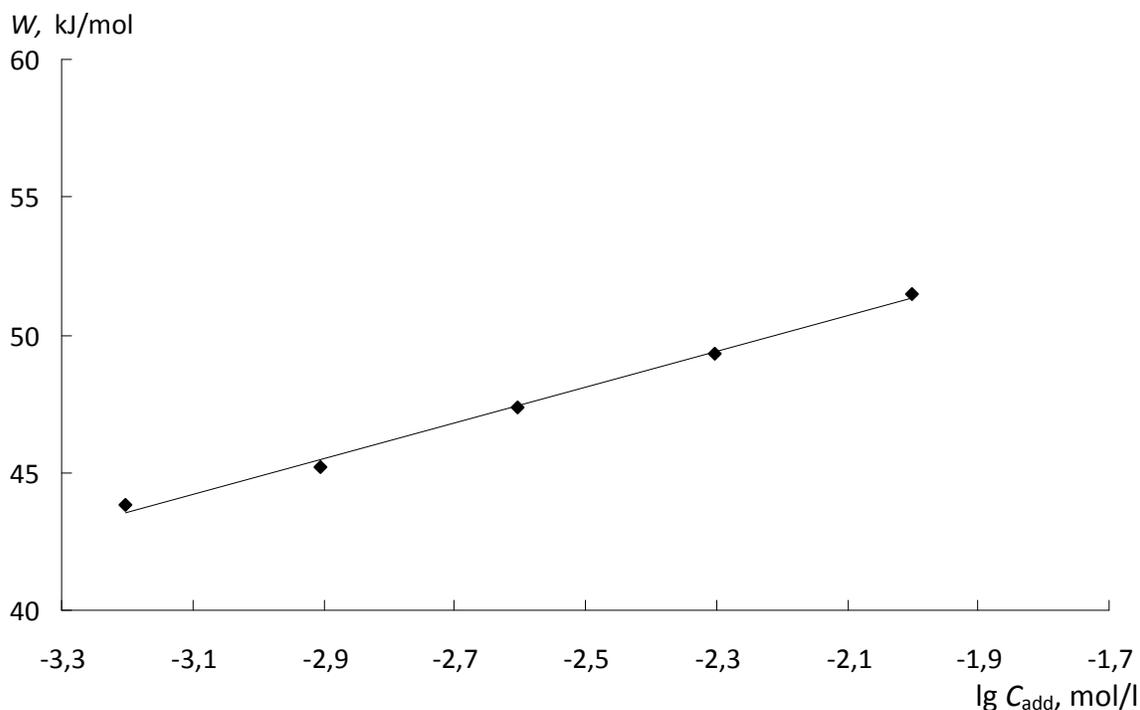


**Fig. 6.** Dependence of  $\lg j$  on  $1/T$  in the case of Al corrosion in 1 M  $H_2SO_4$  in the presence of the *o*-hydroxyazomethine derivative ( $R = COOH$ ) at concentrations  $C \cdot 10^3$ , mol/l: 0 – 0; 1 – 0.625; 2 – 1.25; 3 – 2.5; 4 – 5.0; 5 – 10.0.

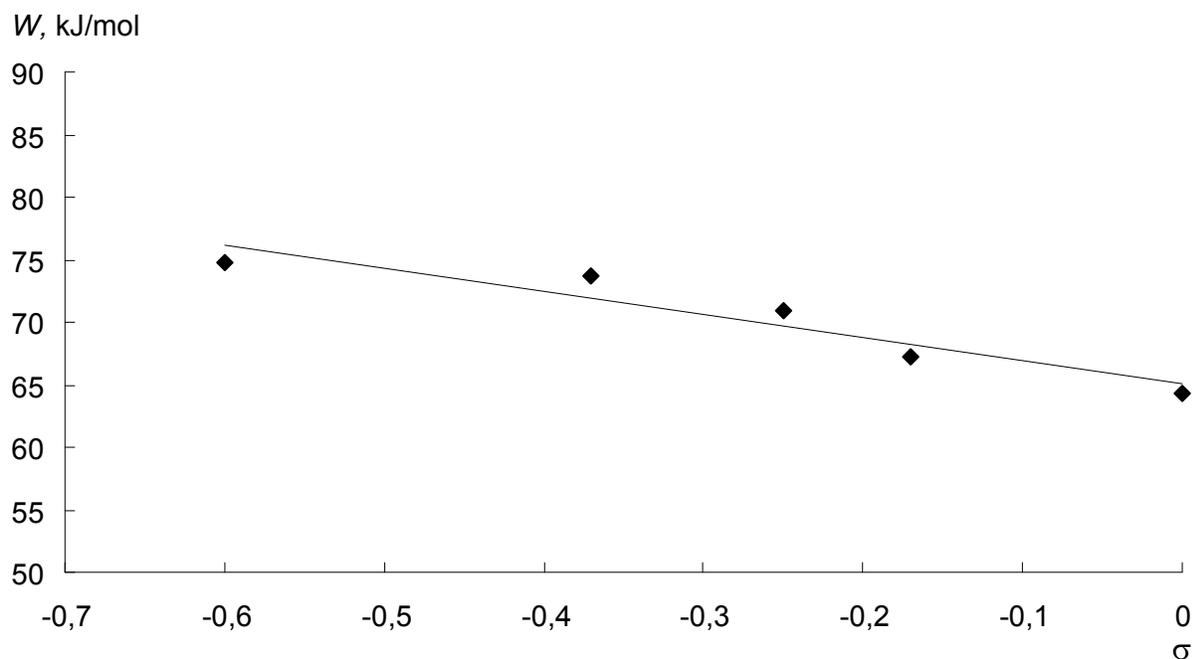
solution temperature, the more quickly  $C_s$  decreases to some limit, after which it changes rather slowly. Moreover, the higher the temperature of the reference solution, the faster the decrease in  $C_s$  to a certain limit and the smaller this limit. The abrupt change in the character of the  $C_s = f(t)$  relationship depending on the temperature of the reference solution may be due to a change in the character of adsorption forces between Al and the inhibitor as the inhibitor is removed from the Al electrode surface. It can be expected that the physically adsorbed inhibitor molecules will be preferentially removed at first, whereas chemisorbed molecules will be removed at the subsequent stages. Possibly, this is reflected by the inflexion on the  $C_s = f(t)$  plots.

Given the known dependence of activation energy  $W$  for Al corrosion *versus* the concentration of the inhibitor with  $R = COOH$ , Fig. 10, and the dependence of the

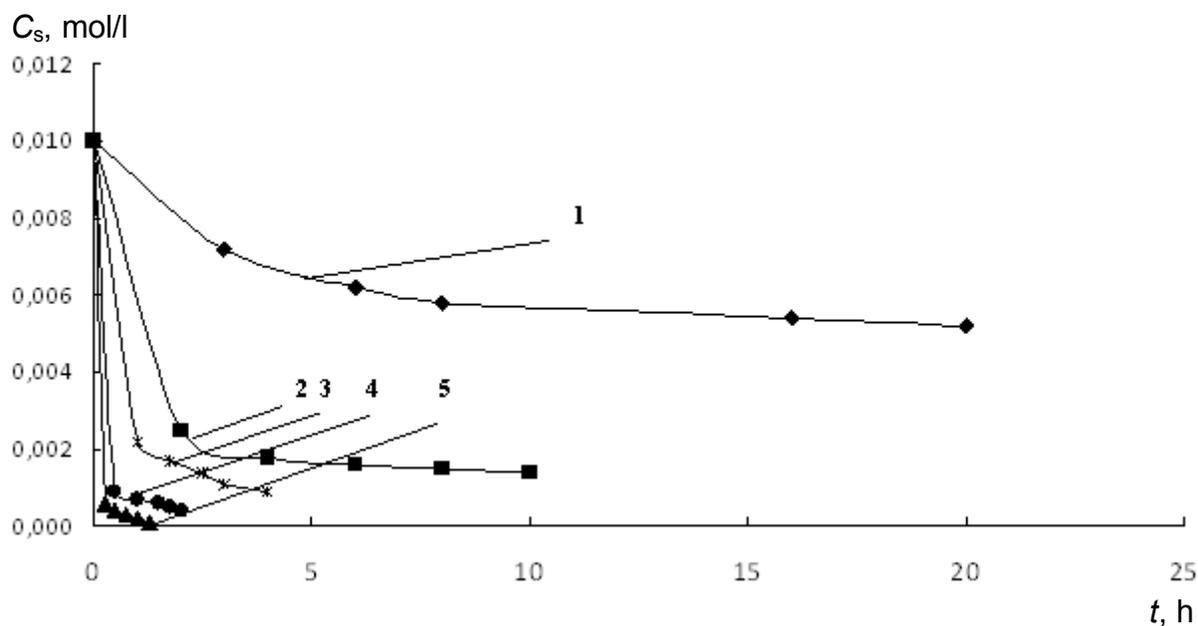
concentration  $C_s$  near the electrode *versus* time for the reference solution at various temperatures, one can find the relationship  $W_s = f(t)$  for each temperature of the reference solution, Fig. 11. It follows from the figure that immersion of an Al electrode pretreated with the inhibitor into reference solutions with various temperatures results in an abrupt  $W$  decrease with time, which is the stronger the higher the temperature. This reflects a decrease in the protective properties of the pre-adsorbed inhibitor film. However, activation control of the corrosion process is observed in the entire experimental time range studied.



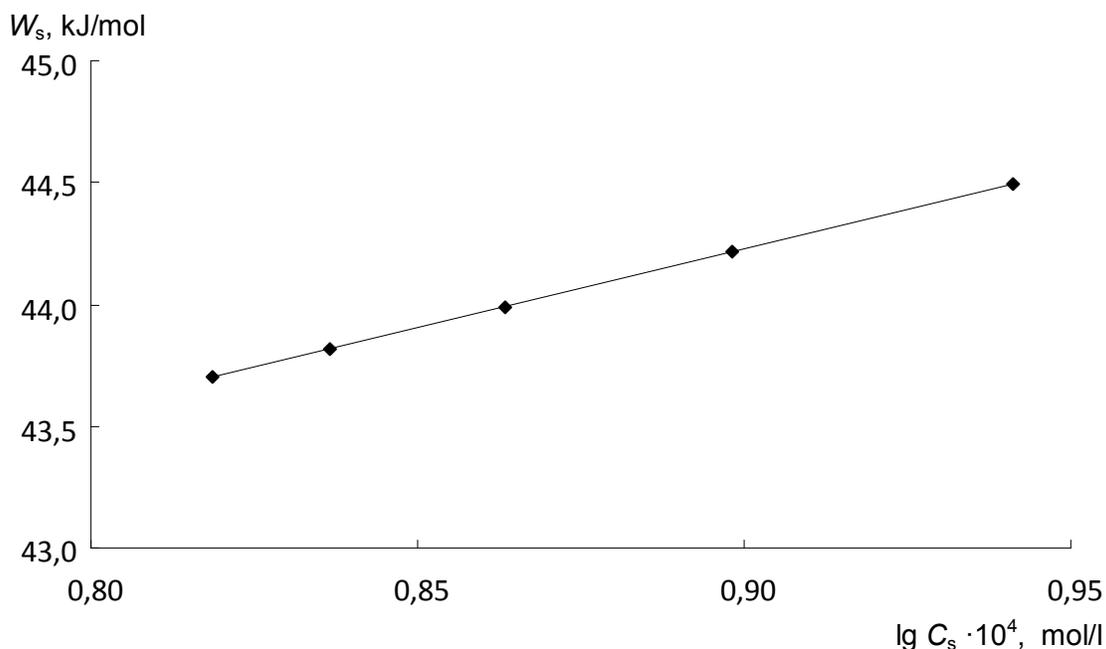
**Fig. 7.** Dependence of effective activation energy of Al corrosion in 1 M  $\text{H}_2\text{SO}_4$  on the concentration of the *o*-hydroxyazomethine derivative ( $\text{R}=\text{COOH}$ ).



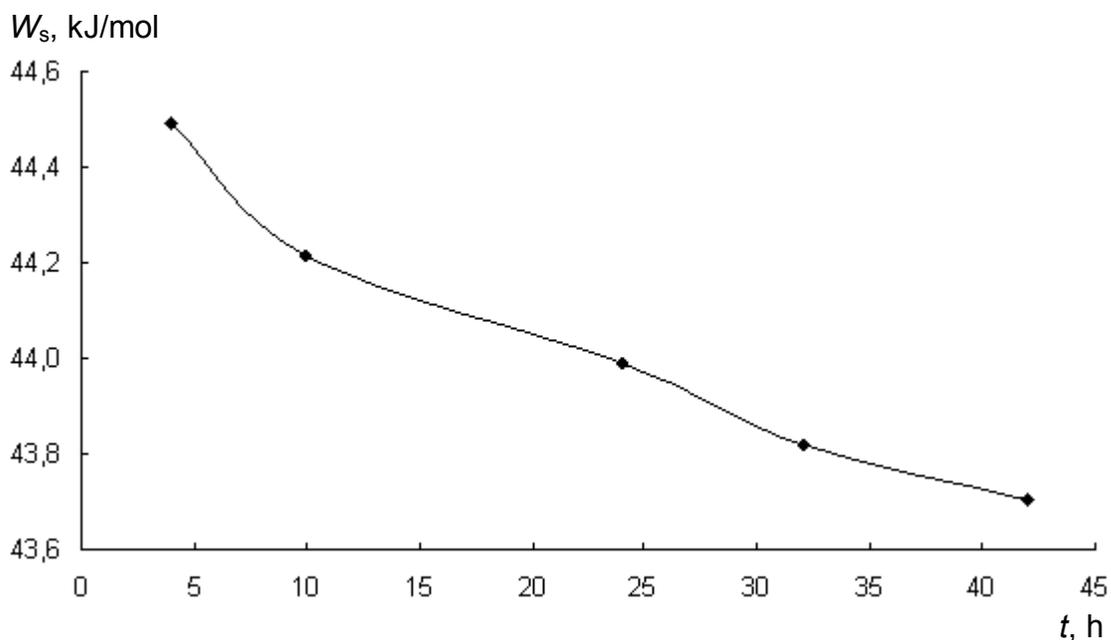
**Fig. 8.** Plot of effective activation energy of Al corrosion in 1 M  $\text{H}_2\text{SO}_4$  versus the polarity  $\sigma$  of the substituents in the molecules of individual *o*-hydroxyazomethine derivatives in 1 M  $\text{H}_2\text{SO}_4$ .



**Fig. 9.** Plot of the near-electrode concentration of the *o*-hydroxyazomethine derivative with  $R = \text{COOH}$  after its pre-adsorption on Al electrodes versus immersion time of these electrodes in 1 M  $\text{H}_2\text{SO}_4$  at: 1 – 20; 2 – 30; 3 – 40; 4 – 50; 5 – 60°C.



**Fig. 10.** Plot of the effective activation energy under RPE conditions for Al electrode in 1 M  $H_2SO_4$  pretreated with the *o*-hydroxyazomethine derivative with  $R = COOH$  versus the near-electrode concentration in 1 M  $H_2SO_4$ .

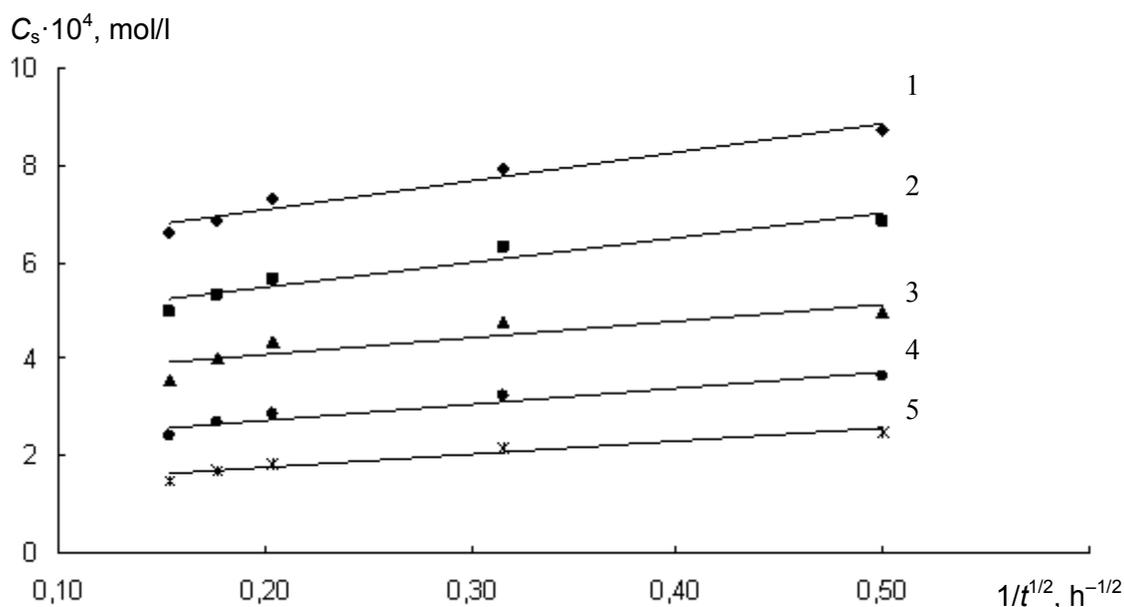


**Fig. 11.** Plot of the effective activation energy under RPE conditions for Al electrode in 1 M  $H_2SO_4$  pretreated with the *o*-hydroxyazomethine derivative with  $R = COOH$  versus immersion time in 1 M  $H_2SO_4$ .

Apparently, prolonged preservation of the RPE by a pre-formed adsorption film is possible provided that a strong bond exists between the adsorbed inhibitor molecules and

the metal surface. For this reason, this effect should be expected in the case of chemisorbed inhibitor molecules, as mainly observed for transition metals and inhibitor molecules with very mobile unsaturated electron systems (bonds). The RPE should be smaller in the case of non-transition metals where physical adsorption of an inhibitor usually predominates and a considerable role is played by electrostatic attraction between the metal and the inhibitor, which, among other factors, is determined by the  $\phi$ -potential and the sign of charges of the metal and the adsorbing inhibitor molecule [7].

It should be noted in conclusion that under the RPE conditions studied, the non-steady-state character of inhibitor desorption from the metal surface, the rate of which increases with an increase in temperature, is additionally demonstrated by the linear plot of  $C$  versus  $1/\sqrt{t}$ , Fig. 12. The latter is typical of various non-steady-state processes (e.g., a decrease in current with time in the case of cathodic deposition of metals, a decrease in heat release in the case of metal cooling, etc.).



**Fig. 12.** Plot of the near-electrode concentration of the *o*-hydroxyazomethine derivative with  $R = \text{COOH}$  under RPE conditions for Al versus immersion time in 1 M  $\text{H}_2\text{SO}_4$  after treatment in pre-adsorption solutions at the following concentrations: 1 – 10.0; 2 – 5.0; 3 – 2.5; 4 – 1.25; 5 –  $0.625 \cdot 10^3$  mol/l.

## Conclusions

1. The time variation of the residual protective effect of *o*-hydroxyazomethine derivatives with various polarity of substituents in the molecules, both as individual compounds and in mixtures, can be interpreted in terms of the LFE principle.
2. The duration of residual protective effect of *o*-hydroxyazomethine derivatives in acid corrosion of aluminum linearly depends on the polarity of the substituents, the inverse

absolute temperature of the solution, and the logarithm of inhibitor concentration in the pre-adsorption solution.

3. The near-electrode concentration of the additive desorbed from the Al electrode surface is described as a function of time from the start of desorption and solution temperature. Based on this, the change in the effective activation energy of Al corrosion during inhibitor desorption was estimated as a function of time.
4. The residual protective effect of *o*-hydroxyazomethine derivatives against corrosion of Al and Fe in 1 M H<sub>2</sub>SO<sub>4</sub> depends on external factors ( $\sigma$ ,  $C$ ,  $T$ ) in a similar way for both metals.

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