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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

N', *N*'-Dialkylhydrazides as Inhibitors of Acid Corrosion of Steel

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Abstract—The effect of *N*',*N*'-dialkylhydrazides of aliphatic carboxylic acids of the general formula $C_4H_9CH(C_2H_5)C(O)NHN(R)_2$ on the corrosion behavior of St.20 steel in 0.1 and 1 M HCl was studied by electrochemical and gravimetric methods.

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Corrosion of metal alloys causes enormous damage to both the industry and the environment. Annual metal loss reaches 12% of the total metal stock, or 30% of the annual metal production [1]. Therefore, search for new inhibitors remains an urgent problem. Among *N*',*N*'-dialkylhydrazides of aliphatic carboxylic acids (DAHCAs), *N*',*N*'-dialkylhydrazide of 2-ethylhexanoic acid (DAH-2EHA) was tested as inhibitor of acid corrosion. It is known that some hydrazides are used as drugs [2], in polymer synthesis [3], as extractants for nonferrous and rare metals [4], as collectors in KCl flotation [5], and as corrosion inhibitors [6].

It was shown previously [7] that the inhibiting effect of hydrazides of fatty carboxylic acids (HFAs) in 0.1 M HCl was manifested with C_7–C_8 substituents, and at R = C_9–C_{12} it amounted to 82–96%, whereas in neutral media hydrazides with R = C_7H_{15} and $C_{10}H_{21}$ acted as corrosion stimulants, and for C_8H_{17} and $C_{12}H_{25}$ the protective effect did not exceed 11%.

N',*N*'-Dialkyl- and *N*',*N*'-dibenzylhydrazides of 2-ethylhexanoic acid (DAH-2EHA) of the general formula $C_4H_9CH(C_2H_5)C(O)NHN(R)_2$, where R = C_2H_5, C_4H_9, C_5H_{11}, C_8H_{17}, $CH_2C_6H_5$, and $C_4H_9CH(C_2H_5)CH_2$ were prepared by the reaction of the unsubstituted acid hydrazide with a twofold (by moles) amount of the corresponding alkyl bromide in the presence of KOH. The synthesis was performed in i-PrOH with the addition of benzene for azeotropic distillation of water. The mixture was refluxed for 15 h. Then the KBr precipitate was filtered off, the alcohol was distilled off, and the residue was dissolved in chloroform. The organic layer was washed with water and a sodium carbonate solution. The products were recrystallized from acetone–water mixtures (3 : 1 to 7 : 1). 2-Ethylhexanoic acid *N*',*N*'-di(2-ethylhexyl)hydrazide was purified by transforming it into salicylate, with the subsequent neutralization with ammonia. The product purity was confirmed by TLC, IR and ^{1}H NMR spectroscopy, and analysis by nonaqueous potentiometric titration [8] and volumetric heterophase titration with sodium lauryl sulfate [9]. The main substance contents and melting points of the hydrazides are listed in Table 1.

Corrosion tests were performed with samples made of St.20 steel. Gravimetric tests were performed with flat samples of size 30 × 20 × 2 mm, and electrochemical studies, with flat electrodes with a working surface area of 1 cm^2. Sample pretreatment involved trimming with fine abrasive papers, degreasing with alcohol, and washing with distilled water. In gravimetric tests, the whole surface of the samples was exposed to the solution, and in electrochemical tests all nonworking surfaces were insulated with a wax–rosin mixture. The tests were performed in 0.1 and 1 M HCl (chemically pure grade). Working electrolytes were prepared in distilled water. An inhibitor sample was dissolved in the corrosion medium, after which the protective action Z and inhibiting effect γ were estimated gravimetrically [7] using the formulas

$$Z = \frac{\rho_0 - \rho}{\rho_0}\, 100 = \frac{i_0 - i}{i_0}\, 100, \qquad (1)$$

$$\gamma = \frac{\rho_0}{\rho}\,, \qquad (2)$$

where ρ_0 and ρ are the rates of steel corrosion without inhibitor and with its addition (g m^{-2} h^{-1}), respectively, and i_0 and i are the corrosion current densities (A m^{-2}) without inhibitor and with its addition, respectively.

To estimate the polarization resistance, examine the mechanism of the action of organic additives and their effect on electrochemical processes occurring on the steel surface in acids, and determine the rate of steel corrosion i_{cor}, we used the method of polarization curves. The curves were recorded with a PI-50 potentiostat in a YaSE-2 standard electrochemical cell with a saturated silver chloride reference electrode and a platinum auxiliary electrode. The working electrode was placed in the cell with the electrolyte being tested and kept there for 30 min to attain a constant corrosion potential E_{cor}. The cathodic and anodic polarization curves were taken in the potentiostatic mode with a step of 20 mV. The time of keeping the system at each potential was 1 min. When estimating the polarization resistance for taking the U–I characteristics, we chose the potential interval of ±30 mV relative to the corrosion potential. The curves were taken in the potentiostatic mode with a step of 3–4 mV in the direction from cathodic to anodic region, with keeping for 1 min at each potential. The polarization resistance R_p was calculated as the slope of the tangent to the polarization curves in the point corresponding to $i = 0$.

The corrosion current was calculated by the equation

$$i_{cor} = \frac{b_c\ b_a}{2.3\,(b_c + b_a)}\frac{1}{R_p} = \frac{B}{R_p}, \qquad (3)$$

where b_c and b_a are the coefficients of the Tafel equation, determined from the results of the polarization measurements.

The data presented in this paper were obtained by averaging the results of three to four measurements.

In the first step of our study, we determined gravimetrically the rate of St.20 corrosion in 0.1 and 1 M HCl with additions of DAH-2EHA and without them. The concentration of the hydrazides in solutions was varied within 0.02–0.05 g l^{-1} in 0.1 M HCl and 0.02–0.1 g l^{-1} in 1 M HCl, which is determined by the solubility of these compounds in aqueous media [9]. The results of the tests are given in Table 2. As can be seen, in 0.1 M HCl, addition of 0.02 g l^{-1} hydrazide does not noticeably affect the rate of St.20 corrosion. The protective effect becomes noticeable at a hydrazide concentration of 0.05 g l^{-1}, amounting to approximately 60% for R = C_4H_9, C_5H_{11}, and $CH_2C_6H_5$, which is associated with an increase in the length of the hydrocarbon radical in the case of R = C_4H_9 and C_5H_{11} and with the presence of an aromatic ring in $CH_2C_6H_5$.

The maximal protective effect Z in 1 M HCl at 0.1 g l^{-1} concentration of the additives was 50–70%. The best results at both HCl concentrations were obtained with R= C_2H_5, C_4H_9, C_5H_{11}, and $CH_2C_6H_5$, and therefore these derivatives were taken for further electrochemical studies.

Figures 1a and 1b show the polarization curves (PCs) taken on St.20 in 0.1 and 1 M HCl without inhibitor and in the presence of DAH-2EHA with R = $CH_2C_6H_5$. It can be seen that in all the cases a Tafel dependence is observed, and introduction of hydrazides in various concentrations inhibits both processes. The results of treatment of the PCs taken in the presence of DAH-2EHA are given in Table 3. It can be seen that the DAH-2EHA inhibitors affect both steps of the corrosion process, shifting the corrosion potential toward more positive values, decreasing the corrosion rate, and favoring an increase in the Tafel slopes of both the cathodic and anodic curves. Intense polarization of the electrode gives rise to various factors that can distort the results of corrosion tests: dissolution of the electrode surface, leading to an increase in the true surface area; formation of corrosion products; change in the electrolyte composition; and additional cathodic currents at intense polarization. This can be avoided by using the polarization resistance method

Table 1. Main substance contents and melting points of hydrazides $C_4H_9CH(C_2H_5)CONHNR_2$

R	Empirical formula	*M*	Main substance content, wt %	T_m, °C
C_2H_5	$C_{12}H_{26}N_2O$	214.4	98	78.5–79.0
C_4H_9	$C_{16}H_{34}N_2O$	270.5	99	75.0–75.5
C_5H_{11}	$C_{18}H_{38}N_2O$	298.5	99	70.0–75.5
C_8H_{17}	$C_{24}H_{50}N_2O$	382.7	100	43.0–43.5
$CH_2C_6H_5$	$C_{22}H_{30}N_2O$	338.5	98	99.0–99.5
$C_4H_9CH(C_2H_5)CH_2$	$C_{24}H_{50}N_2O$	382.7	96	46.0–48.0

Table 2. Corrosion rate of St.20 in 0.1 and 1 M HCl and protective (Z) and inhibiting (γ) effects of hydrazides $C_4H_9CH(C_2H_5)CONHNR_2$

	Hydrazide concentration, g l^{-1}						Hydrazide concentration, g l^{-1}					
	0.02			0.05			0.05			0.1		
	ρ, g m^{-2} h^{-1}	Z, %	Y	ρ, g m^{-2} h^{-1}	Z, %	Y	ρ, g m^{-2} h^{-1}	Z, %	Y	ρ, g m^{-2} h^{-1}	Z, %	Y
	0.1 M HC1						1 M HC1					
Corrosion medium	1.10	–	–	1.34	–	–	8.67	–	–	8.67	–	–
H	1.05	4	1.0	1.19	12	1.1	8.16	6	1.05	6.95	20	1.2
C_2H_5	0.96	13	1.1	1.03	23	1.3	6.65	23	1.3	6.65	23	1.3
C_4H_9	1.00	9	1.1	0.56	58	2.40	5.56	36	1.66	4.10	53	2.11
C_5H_{11}	0.96	13	1.1	0.50	63	2.68	3.81	56	2.27	2.34	73	3.71
C_8H_{17}	1.03	6	1.0	1.19	12	1.1	8.78	–	–	8.49	–	–
$C_4H_9CH(C_2H_5)CH_2$	0.96	13	1.1	1.41	–	–	6.73	22	1.28	6.42	26	1.4
$CH_2C_6H_5$	0.92	16	1.2	0.51	62	2.62	5.58	36	1.55	4.52	48	1.92

Table 3. Corrosion-electrochemical characteristics of St.20 in 0.1 and 1 M HCl in the presence of inhibitors $C_4H_9CH(C_2H_5)CONHNR_2$

R	0.1 M HCl + 0.05 g l^{-1} inhibitor					1 M HCl + 0.1 g l^{-1} inhibitor				
	E_{cor} (vs. AgCl/Ag)	b_c	b_a	i_{cor}, A m^{-2}		E_{cor} (vs. AgCl/Ag)	b_c	b_a	i_{cor}, A m^{-2}	
	V			from PC	by Eq. (3)	V			from PC	by Eq. (3)
Corrosion medium	−0.48	0.12	0.06	1.24	1.24	−0.470	0.100	0.09	2.2	2.1
C_2H_5	−0.47	0.16	0.10	1.00	1.0	−0.465	0.140	0.120	1.5	1.7
C_4H_9	−0.45	0.14	0.08	0.89	0.89	−0.440	0.140	0.09	1.6	1.6
$C_5 H_{11}$	−0.45	0.18	0.10	0.79	0.79	−0.460	0.120	0.100	1.5	1.7
$CH_2C_6H_5$	−0.47	0.16	0.12	0.76	0.76	−0.460	0.100	0.110	1.6	1.5

Table 4. Protective effect of inhibitors $C_4H_9CH(C_2H_5)CONHNR_2$ in 1 and 0.1 M HCl from the results of gravimetric and electrochemical measurements

R	Protective effect Z, %			
	1 M HCl + 0.1 g l^{-1} inhibitor		0.1 M HCl + 0.05 g l^{-1} inhibitor	
	electro-chemistry	gravimetry	electro-chemistry	gravimetry
C_2H_5	19	23	20	23
C_4H_9	28	52	37	58
$C_5 H_{11}$	24	73	37	61
$CH_2C_6H_5$	16	47	40	62

[10]. Comparison of the corrosion currents obtained by extrapolation of the Tafel portions and calculated by the method of polarization resistance [Eq. (3)] (Table 3) shows that the results are in good agreement.

The protective effects determined from the electrochemical and gravimetric measurements are given in Table 4. It can be seen that the absolute values determined gravimetrically and calculated from the electrochemical measurements do not coincide. This is due to the following facts. The gravimetric measurements give the corrosion rate averaged over the experimental period (24 h), whereas in electrochemical measurements these parameters are determined at a specific instant of time. As the action of an inhibitor involves the occurrence in time of adsorption processes on the electrode surface, the results of the gravimetric measurements should be considered to be more reliable. However, the general trends observed in the electrochemical and gravimetric measurements coincide. In both cases, the hydrazides with R = C_5H_{11} and $CH_2C_6H_5$ are the most effective. On the whole, the low values of the inhibiting and protective effects of the DAH-2EHAs are most probably due to their relatively low adsorption. An increase in the length and degree of branching of the hydrocarbon radical leads to an increase in the inhibiting power (increase in protective effects in going from R = C_2H_5 to R = C_5H_{11} and $CH_2C_6H_5$). The compounds with R = C_8H_{17} and $CH_2CH(C_2H_5)C_4H_9$ might have better characteristics if they were better soluble in HCl solutions. It is known [11] that, similarly to unsubstituted aliphatic acid hydrazides [12], the hydrazides under consideration (HL) are amphoteric and form organic cations (H_2L^+) in acid solutions:

$$\mathrm{H_2L^+} \xrightleftharpoons{-\mathrm{H^+},\ \mathrm{p}K_{\mathrm{a1}}} \mathrm{HL} \xrightleftharpoons{-\mathrm{H^+},\ \mathrm{p}K_{\mathrm{a2}}} \mathrm{L^-}. \tag{4}$$

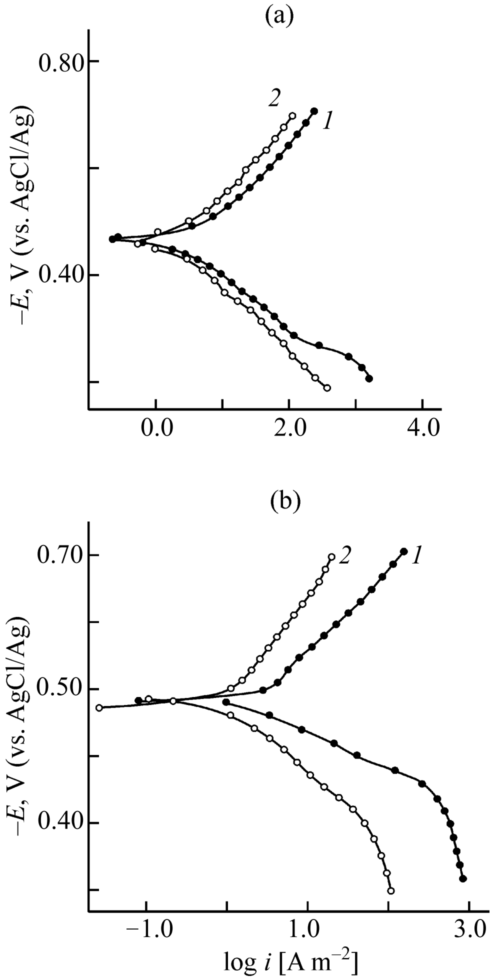
A study of the effect of organic cations on partial electrode reactions determining the iron corrosion in acids shows that the corrosion deceleration in this case is due to an increase in the overvoltage of electrode reactions as a result of an increase in the positive value of the adsorption ψ' potential [13]. In view of the large size of cations of protonated DAH-2EHAs, it can be assumed that the mechanism of their action as inhibitors is mixed, i.e., the contribution of mechanical shielding of the surface in adsorption of these additives should also be taken into account.

Thus, the examined compounds are complex inhibitors, and their protective effect is due to a number of factors, including the ψ' effect and the blocking effect.

CONCLUSIONS

(1) 2-Ethylhexanoic acid N',N'-dialkylhydrazides are mixed-type (cathodic–anodic) inhibitors of acid corrosion of St.20 steel in 0.1 and 1 M HCl, decreasing the rates of both anodic and cathodic processes.

(2) The protective effect of these compounds increases with an increase in the length of the hydrocarbon radical. Enhancement of the protective effect in going from R = C_2H_5 to R = C_5H_{11} and $CH_2C_6H_5$ is due to an increase in the adsorption of these compounds as a result of an increase in the length and degree of branching of the radical.



Polarization curves taken on St.20 in (a) 0.1 and (b) 1 M HCl. (*E*) Potential and (*i*) current density. (*1*) No inhibitor and (*2*) DAH-2EHA with R = $CH_2C_6H_5$ added in an amount of (a) 0.05 and (b) 0.1 g l^{-1}.

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