## APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

# Anticorrosive Properties of N-Acetylmethylpyridinium Bromides

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**Abstract**—The inhibiting action of *N*-acetylmethylpyridinium bromides on the corrosion of low-carbon steel in a 3 M sulfuric acid solution at 20, 40, 60, and 80°C was studied. The mechanism of their protective action was examined using electrochemical methods. Compounds exhibiting high anticorrosive properties at elevated temperatures were found.

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It has been shown previously [1] that *N*-phenacylmethylpyridinium bromides (**A**) are effective inhibitors of the acid corrosion of steel and their protective properties depend on the nature of the substituents R and  $R^1$ :



It was found, by varying R and R<sup>1</sup>, that the coefficients  $\gamma$  of steel corrosion hindrance for these compounds at 20 and 40°C correlate with the  $\sigma_c^0$  constants characterizing the combined action of the mesomeric and  $\pi$ -induction effects of the substituents R and with the induction  $\sigma_I$  constants of R<sup>1</sup> groups. As temperature increases, their anticorrosive action is significantly enhanced, but, in this case, the correlation between the corrosion hindrance factors and the electronic characteristics of the substituents is broken.

This study is concerned with the anticorrosive properties of pyridinium bromides containing a  $CH_3$  or  $NH_2$  group in position 2 and methylacyl groups with  $CH_3$ , *t*-Bu, 1-Ad, and 2-thienyl substituents at the nitrogen atom (compounds **Ia–Id**, **IIa–IId**):



where  $R = CH_3$  (I),  $NH_2$  (II);  $R^1 = CH_3$  (a), *t*-Bu (b), 1-Ad (c), 2-thienyl (d).

The pyridinium bromides necessary for the study were synthesized by the standard procedure involving the reaction of 2-methyl- or 2-aminopyridine with the corresponding bromomethyl ketones.

## EXPERIMENTAL

The anticorrosive properties of the compounds studied were evaluated at inhibitor concentrations of  $1 \times 10^{-2}$  M by the corrosion hindrance factors  $\gamma$  and degrees Z of corrosion protection of 08KP steel in a 3 M sulfuric acid solution at 20, 40, 60, and 80°C. The corrosion tests were carried out using the conventional gravimetric method [1]. Voltammetric measurements were performed in the potentiodynamic mode, after a free corrosion potential  $E_c$  of steel is attained, at a potential sweep rate of 2 mV s<sup>-1</sup>.

The results obtained in the corrosion tests demonstrated that compounds **Ia–Id** and **IIa–IId** exhibit a stronger inhibiting effect than their phenacyl analogs **Ie** and **IIe** (Table 1). For compounds **Ie** and **IIe** at 20°C, the steel corrosion hindrance factors are 15.50 and 23.70, respectively [1]; and for compounds **Ia–Id** and **IIa–IId**, 19.60–39.60. As temperature increases, the anticorrosive effect of the compounds studied is enhanced, and at 60°C the hindrance factors are approximately 200–560 and 200–860 for compounds **Ia–Id** and **IIa–IId**; for their phenacyl analogs, the hindrance factors do not exceed 200 units.

It is known that, owing to the methylene group separating the pyridinium and phenacyl moieties, the compounds under study exhibit a conformational lability, which allows them to occupy, depending on conditions, a position on the steel surface that is the **Table 1.** Hindrance factors  $\gamma$  and degree Z of corrosion protection of 08KP steel in a 3 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of *N*-acetylmethylpyridinium bromides



Com- pound	R	R <sup>1</sup>	20°C		40°C		60°C		80°C	
			γ	Z, %	γ	Z, %	γ	Z, %	γ	Z, %
Ia Ib Ic Id	CH <sub>3</sub> CH <sub>3</sub> CH3 CH3 CH <sub>3</sub>	$\overbrace{C(CH_3)_3}^{CH_3}_{1-Ad}$	19.60 22.50 23.70 19.10	94.90 95.56 95.58 94.76	22.00 36.40 31.90	95.45 97.25 96.86	216.23 297.31 317.13 559.60	99.54 99.66 99.68 99.82	59.8 - 157.00 369.86	98.33 99.36 99.73
Ie IIa IIb IIc IId	$\begin{array}{c} \mathrm{CH}_3 \\ \mathrm{NH}_2 \\ \mathrm{NH}_2 \\ \mathrm{NH}_2 \\ \mathrm{NH}_2 \\ \mathrm{NH}_2 \end{array}$	$\overbrace{C_{6}H_{5}}^{C_{6}H_{5}}$ $C(CH_{3})_{3}$ $1\text{-Ad}$ $\swarrow$ $S$	15.50 32.00 34.62 39.60 24.30	93.54 96.88 97.11 97.47 95.88	18.70 40.50 39.10 43.00 35.40	94.65 97.53 97.44 97.67 97.18	209.10 218.70 339.79 413.70 864.90	99.52 99.54 99.71 99.76 99.88	150.40 68.00 - 273.70 651.66	99.34 98.53 - 99.63 99.85
IIe	NH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	23.70	95.78	29.00	96.55	200.30	99.50	144.60	99.31

most favorable for adsorption. As also in pyridinium bromides **Ie**, **IIe** [1], the most probable reaction center responsible for adsorption of the compounds under study at room temperature is the pyridinium moiety of the molecule, which gives rise to a positive adsorption-related step of the potential and hinders corrosion by the energy mechanism of inhibition. At the same time, the carbonyl group contained in these compounds is responsible for chemisorption of the compounds, which becomes more pronounced as the solution temperature increases [2].

It was found that compounds **Ia–Ic**, **Ie**, **IIa–IIc**, and **IIe** at 20°C show linear relationships between  $\log \gamma$  and the induction  $\sigma^*$  constants of the substituents R<sup>1</sup>:

$$\log \gamma = 1.30 - 0.174\sigma^* R^1, \ r = 0.999,$$
 (1)

$$\log \gamma = 3.45 - 0.455\sigma^* R^1, \ r = 0.991.$$
 (2)

The coefficients (0.174 and 0.455) in Eqs. (1) and (2) point to different sensitivities of the adsorption centers in compounds **Ia–Ic**, **Ie** and **IIa–IIc**, **IId** to the induction effect of the substituents  $\mathbb{R}^1$ . This may be due to difference in the induction and mesomeric effects of the methyl and amino groups on the polari-

zability of the compounds and, consequently, on their adsorbability on the steel surface. It should also be noted that compounds **Id** and **IId** are not described by the dependences obtained and their inhibiting effect is considerably stronger than that expected with account of only the strength and type of the induction effect of the 2-thienyl radical. Such a behavior of inhibitors Id and IId can be attributed on the assumption that not only the main adsorption centers, but also the thiophene ring directly interact with the steel surface, as previously observed in [3]. As temperature increases, the linear relations  $\log \gamma - \sigma^* R^1$  cease to be valid, which may occur for various reasons: transition from physical sorption to chemisorption; change of the mechanism of the protective action of the inhibitors; high rate of steel dissolution, which hinders their adsorption on the metal; and some other factors. In this case, the correlation coefficients decrease to 0.939, 0.936 at 40°C and 0.877, 0.886 at 60°C.

Quantum-chemical calculations of the charge distribution within the molecule were carried out for compounds **Ia–Ie** and **IIa–IIe** (Table 2). The molecular configurations were optimized by the B3LYP method [4] with the standard 6-31G basis set, using the GAUSSIAN software package [5]. All the stationary points were characterized via a complete analysis

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	<i>q</i>										
Compound*	N <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	C <sup>8</sup>	O <sup>9</sup>	N <sup>10</sup>	S <sup>10</sup>	S <sup>11</sup>
I:	1		1					1	1		
$\mathbf{R} = \mathbf{CH}_3$ (a)	-0.295	0.078	-0.244	-0.126	-0.233	0.296	0.597	-0.516	_	_	_
$\mathbf{R} = t - \mathbf{B}\mathbf{u}$ ( <b>b</b> )	-0.296	0.075	-0.243	-0.126	-0.233	0.295	0.607	-0.526	-	—	_
R = 1-Ad (c)	-0.295	0.074	-0.244	-0.127	-0.233	0.294	0.610	-0.530	-	_	-
$\mathbf{R} = \overbrace{\mathbf{S}}^{\mathbf{S}}(\mathbf{d})$	-0.296	0.077	-0.244	-0.125	-0.234	0.300	0.518	-0.545	_	0.477	_
R = Ph (e) II:	-0.295	0.078	-0.244	-0.126	-0.233	0.296	0.552	-0.541	_	_	-
$\mathbf{R} = \mathbf{CH}_3$ (a)	-0.348	0.060	-0.269	-0.129	-0.278	0.466	0.599	-0.541	-0.806	_	_
$\mathbf{R} = t - \mathbf{B}\mathbf{u}$ ( <b>b</b> )	-0.347	0.060	-0.272	-0.131	-0.278	0.465	0.619	-0.551	-0.803	_	_
$\mathbf{R} = 1 \text{-} \mathbf{A} \mathbf{d}  (\mathbf{c}$	-0.346	0.061	-0.273	-0.132	-0.279	0.465	0.629	-0.556	-0.804	-	-
$\mathbf{R} = \overbrace{\mathbf{S}(\mathbf{d})}^{\mathbf{R}}$	-0.351	0.059	-0.275	-0.134	-0.280	0.466	0.524	-0.572	0.800	_	0.488
$\mathbf{R} = \mathbf{P}\mathbf{h}  (\mathbf{e})$	-0.351	0.059	-0.274	-0.133	-0.279	0.465	0.563	-0.573	-0.802		
* 4		4									

Table 2. Charges q in compounds Ia–Id and IIa–IId



of the normal modes of harmonic vibrations, in which NIMAG = 0 corresponds to minima on the potential energy surface for all of the optimized structures. The calculations demonstrated that, as the substituents  $R^1$  in the compounds studied are varied, the effective charges on the respective atoms within each series remain virtually the same and change only slightly on passing from **Ia–Id** to **IIa–IId**. The only exception are charges on  $\alpha$ -carbon atoms of the pyridine ring (C<sup>6</sup>), which strongly differ between the series **I** and **II**. This is due to the different electronegativities of the carbon and nitrogen atoms in the CH<sub>3</sub> and NH<sub>2</sub> groups.

The results obtained (Table 1) suggest that an important role in the inhibiting action of acylmethylpyridinium bromides is played by steric factors. In the series of compounds **Ia–Ic** and **IIa–IIc** with CH<sub>3</sub>, *t*-Bu, and 1-Ad groups, for which the steric constants  $E_s^c$  are, respectively, 0.00, -2.40 [6], and -2.68 [7], a correlation between the corrosion hindrance factors and the steric effect exerted by these substituents is observed.

The plots of the dependences  $\log K_{\rm m} - 1/T$  ( $K_{\rm m}$  is the gravimetric corrosion index, and T, absolute temperature) in Fig. 1 indicate that N-acylmethylpyridinium bromides affect the effective activation energy of corrosion. In the temperature range  $20-40^{\circ}$ C, the effective activation energies  $W_c$  increase in the presence of compounds Ia-Ie and IIa-IIe from 81.69 kJ mol<sup>-1</sup> (no inhibitor) to 86.16–102.44 kJ mol<sup>-1</sup>, which points to the activation mechanism of the inhibiting effect. At higher temperatures, a deviation from the linear dependences  $\log K_{\rm m} - 1/T$  is observed and inflections appear, which are probably due to transition from the physical (specific) adsorption of the compounds to chemisorption. The effective activation energy of corrosion decreases to 58.88–26.33 kJ mol<sup>-1</sup> in the presence of compounds Ia-Ic, Ie and to 19.15 and  $9.57 \text{ kJ mol}^{-1}$  for compounds **Id** and **IId**, respectively. This indicates that the inhibition mechanism changes as the temperature increases and the diffusion limitations appearing when reacting particles penetrate across the adsorbed film of an inhibitor play an important role. For these compounds, a noticeable aftereffect is observed, which consists in that their protec-



**Fig. 1.** Temperature dependence of the corrosion rate of 08KP steel in a 3 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of  $1 \times 10^{-2}$  M *N*-acylmethylpyridinium bromides. ( $K_{\rm m}$ ) Gravimetric corrosion index and (*T*) absolute temperature. Inhibitor: (1) none, (2) Ie, (3) Id, and (4) IId.

tive action is preserved after metal samples are removed from the inhibiting medium. For example, the corrosion of steel in a 3 M H<sub>2</sub>SO<sub>4</sub> solution at 60°C in the presence of  $1 \times 10^{-2}$  M **Ic** and **Id** is hindered by factors of 317 and 560, respectively, and that after their being kept in the same solutions for 1 h, washed with distilled water, and submerged in the acid solution without inhibitor at the same temperature, by factors of 30 and 38, respectively.

Voltammetric measurements demonstrated that both the cathodic reaction of hydrogen evolution and the anodic reaction of iron ionization are hindered in the presence of compounds Ic, Id, IIb, and IId (Fig. 2). The presence of these compounds in 3 M H<sub>2</sub>SO<sub>4</sub> solutions affects only slightly the slopes of the cathodic and anodic polarization curves, i.e., has virtually no effect on the mechanism of partial reactions involved in corrosion. Only at weak cathodic polarizations of steel the curves show poorly pronounced regions of limiting current, which are possibly due to the occurrence of concurrent reactions of oxygen ionization or partial reduction of the compounds under study. A stronger change in the slope of the cathodic curve is observed in the presence of compound Id, which possibly indicates that the sulfur atom of the thiophene ring is involved in adsorption. The appearance, in its presence, of a narrow hysteresis loop (Fig. 3) is probably due to hindered desorption from the steel surface of inhibitor molecules or of products



**Fig. 2.** Anodic and cathodic polarization curves measured on 08KP steel in a 3 M  $H_2SO_4$  solution at 20°C in the presence of  $1 \times 10^{-2}$  M of the compounds under study. (*i*) Current density and (*E*) potential (vs. SHE); the same for Fig. 3. Inhibitor: (*1*) none, (*2*) **Ic**, (*3*) **IIc**, (*4*) **Id**, and (*5*) **IIb**.



**Fig. 3.** Anodic and cathodic (forward and back runs) polarization curves measured on 08KP steel in a 3 M  $H_2SO_4$  solution in the presence of  $1 \times 10^{-2}$  M of compounds **Id**, **IIc**. Inhibitor: (1) none, (2) **Id**, and (3) **IIc**.

formed in partial chemical transformations of the inhibitor on the electrode. However, the hindrance factors calculated from the polarization curves satisfactorily coincide for all the compounds with the hindrance factors found in more prolonged gravimetric tests. This indicates that no noticeable chemical transformations of the inhibitors occur at the steel surface at 20°C.

The results of the calculations in Table 3 demonstrated that the corrosion of steel at 20°C in the presence of compounds **Ia**, **Ic**, **Id** and **IIa**, **IIc**, **IId** is hindered by the energy-related and blocking inhibition mechanisms with the predominant contribution of the energy effect. However, the effect of blocking of the metal surface dominates at 60°C, which is indicated by the fact that  $\gamma_{exp}$  markedly exceeds  $\gamma_{\Delta \Psi 1}$  calculated assuming an energy-related inhibition mechanism.

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**Table 3.** Experimentally found  $(\gamma_{exp})$  and calculated  $(\gamma_{\Delta\psi1})$  corrosion hindrance factors of 08KP steel in a 3 M H<sub>2</sub>SO<sub>4</sub> solution for *N*-acylmethylpyridinium bromides **Ia**, **Ic**, **Id**, **IIa**, **IIc**, and **IId** 

Compound, M	T, °C	$\frac{\Delta E_{\rm c}}{{ m mV}}$	γ <sub>exp</sub>	$\gamma_{\Delta \psi 1}$	Ŷθ	
 Ія <sup>.</sup>						
$1 \times 10^{-2}$	20	46	19.60	14.96	1.38	
$4 \times 10^{-3}$	20	45	18.37	13.33	1.37	
$1.6 \times 10^{-3}$	20	15	3.17	2.37	1.34	
$6.4 \times 10^{-4}$	20	6	1.81	1.41	1.28	
$2.56 \times 10^{-4}$	20	2	1.20	1.12	1.07	
Ic.						
$1 \times 10^{-2}$	20	49	23.70	16.78	1.41	
$4 \times 10^{-3}$	20	44	17.31	12.59	1.37	
$1.6 \times 10^{-3}$	20	39	13.04	9.44	1.38	
$6.4 \times 10^{-4}$	20	13	2.34	2.11	1.10	
$2.56  imes 10^{-4}$	20	3	1.18	1.18	1.00	
<b>Id</b> , $1 \times 10^{-2}$	20	46	19.10	14.12	1.35	
<b>Id</b> , $1 \times 10^{-2}$	60	30	559.60	7.14	78.37	
IIa:						
$1 \times 10^{-2}$	20	54	32.00	22.38	1.43	
$4 \times 10^{-3}$	20	48	21.95	15.85	1.38	
$1.6 \times 10^{-3}$	20	29	5.40	5.31	1.02	
$6.4 \times 10^{-4}$	20	14	2.30	2.24	1.03	
$2.56  imes 10^{-4}$	20	8	1.66	1.58	1.05	
IIc:						
$1 \times 10^{-2}$	20	58	39.60	28.18	1.40	
$4 \times 10^{-3}$	20	53	28.13	21.13	1.33	
$1.6 \times 10^{-3}$	20	45	16.91	13.33	1.27	
$6.4  imes 10^{-4}$	20	22	4.45	3.54	1.25	
$2.56 \times 10^{-4}$	20	4	1.28	1.26	1.02	
<b>IId</b> , $1 \times 10^{-2}$	20	50	24.30	17.78	1.37	
<b>Ic</b> , $1 \times 10^{-2}$	60	10	317.13	1.93	164.31	
	1			1	1	

Note: It was taken in the calculations [8] that  $\gamma_{exp} = \gamma_{\Delta\psi1}\gamma_{\theta}$ , where  $\gamma_{\Delta\psi1}$  and  $\gamma_{\Delta\psi1}$  are, respectively, the energy-related and blocking hindrance factors;  $\gamma_{\Delta\psi1} = 10^{K\Delta\psi1}$ ;  $K = b_c/b_0(b_a + b_c)$ ,  $\Delta\psi1 = \Delta E_c/[1 - b_c b_a/b_0(b_a + b_c)]$ ;  $\Delta E_c$ , shift of the free corrosion potential, caused by the inhibitor;  $b_c$  and  $b_a$ , Tafel slopes of the cathodic and anodic polarization curves in a 3 M H<sub>2</sub>SO<sub>4</sub> solution; and  $b_0 = 2.3RT/F$ .

It is also not improbable that the steel corrosion is hindered by the compounds studied by a more complex mechanism, e.g., with a possible reduction of the carbonyl group they contain and subsequent formation of chemisorbed protective films on the metal surface [9].

## CONCLUSIONS

(1) The *N*-acylmethylpyridinium bromides studied are highly effective inhibitors of acid corrosion of steel, especially at elevated temperatures.

(2) The presence in the acyl moiety of the molecule of groups that can be directly involved in an interaction with the steel surface or have a considerable volume markedly enhances the anticorrosive effect of the compounds studied. The hindrance factors at  $60^{\circ}$ C are as large as 414-865 units in separate cases, and the degree of corrosion protection of steel exceeds 99.5% for all of the compounds studied.

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