
Mixtures of pyrilium perchlorate derivatives with sulfur-containing compounds: inhibitors of steel corrosion in sulfuric acid

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Abstract

Gravimetric and electrochemical methods were used to study the effect of 2,6-bis(3-fluoro-4methoxyphenyl)-3-methylpyrilium perchlorate, 2,4-bis(4-ethoxyphenyl)-6-methylpyrilium perchlorate, phenylthiourea, diphenylthiourea, 2-mercaptobenzothiazole (Kaptax), sodium diethyldithiocarbamate, and their binary mixtures on the corrosion of steel in sulfuric acid. It was shown that in a range of concentrations of 10^{-5}–10^{-4} mol/L at a temperature of 25°C, these individual organic compounds decrease the steel corrosion rate. The protective efficiency is 28–94%, depending on the concentration. The efficiency decreases with an increase in temperature, and at temperatures above 60°C, the inhibiting effect changes to stimulation. The compounds studied primarily hinder the cathodic evolution of hydrogen, which is the reason that steel corrosion rate decreases. The efficiency of individual compounds as inhibitors was compared with the calculated characteristics of the molecules. A strong correlation between the protective effect of sulfur-containing additives and the energy difference between the lowest unoccupied and the highest occupied molecular orbitals was revealed. Mixtures of substituted pyrilium perchlorates with sulfur-containing organic compounds were shown to be more efficient inhibitors of steel corrosion. At a temperature of 25°C, the protective effect of the mixtures against steel corrosion is 85–99.7%. The components in the majority of the mixtures were found to enhance the protective properties of each other. It is shown that if a mixture contains sulfuric acid, the effective energy of corrosion activation increases, while the capacitance of the double electric layer decreases. The inhibitor mixtures slow down both electrode reactions.

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Keywords: *acid corrosion, inhibitor mixtures, pyrilium perchlorate, phenylthiourea, diphenylthiourea, mercaptobenzothiazole, sodium diethyldithiocarbamate, sulfuric acid.*

Introduction

Prevention of metal losses in acid treatment is achieved by corrosion inhibitors. Both individual compounds and their mixtures are used as inhibitors. Organic compounds with heteroatoms are known to be the most efficient inhibitors of acid corrosion [1–6].

Components enhance or weaken each other's protective effects. In most cases, mixtures are more efficient than individual compounds [7].

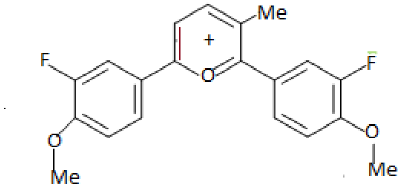
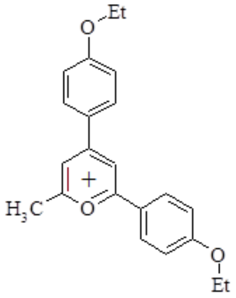
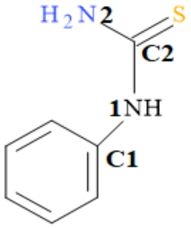
Derivatives of substituted pyrilium perchlorate have been studied as individual inhibitors of the acid corrosion of steel in sulfuric acid [8]. Sulfur-containing organic compounds are used both as corrosion inhibitors and components of inhibitor mixtures [9–11].

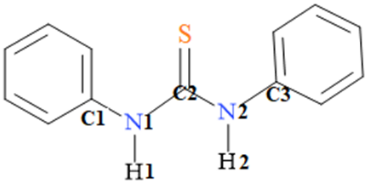
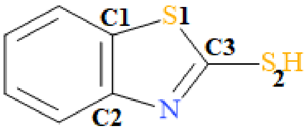
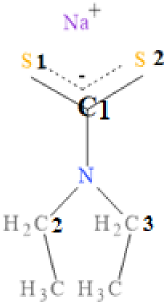
This work aims at studying the protective properties of pyrilium perchlorate derivatives and their mixtures with phenylthiourea, diphenylthiourea, 2-mercaptobenzothiazole (Kaptax), and sodium diethyldithiocarbamate in the acid corrosion of steel in sulfuric acid and comparing the efficiency of additives with the calculated characteristics of the molecules.

Experimental

The compounds presented in Table 1 were studied as steel corrosion inhibitors at a concentration of 10^{-5}–10^{-4} mol/L.

Table 1. The compounds studied.

Formula of compound	Name and notation
 ClO_4^-	2,6-bis(3-fluoro-4-methoxyphenyl)-3-methylpyrilium perchlorate (PP1)
 ClO_4^-	2,4-bis(4-ethoxyphenyl)-6-methylpyrylium perchlorate (PP2)
	Phenylthiourea (PTU)

Formula of compound	**Name and notation**
	Diphenylthiourea (DPTU)
	2-mercaptobenzothiazole (Kaptax)
	Sodium diethyldithiocarbamate (DEDTC)

Preparation of samples and measurement techniques

Samples cut out from low-carbon steel had dimensions of 0.2×1 cm^2 for impedance measurements, 0.5×1 cm^2 for polarization measurements, and 1×2.5 cm^2 for corrosion measurements. Prior to measurements, the samples were cleaned using a sand paper, degreased with alcohol, washed with distilled water, and dried with filtering paper. A 0.5 M solution of sulfuric acid was used as the working electrolyte. Gravimetric measurements were carried out at temperatures of 25, 40, 60, and 80°C.

Corrosion rate K was calculated using the following formula (1)

$$K = \frac{\Delta m}{\tau \cdot S} \tag{1}$$

where Δm is the change in mass (grams), τ is the duration of the experiment (hours), and S is the sample area (m^2).

The efficiency of the additives was evaluated using the inhibition coefficient γ (2) and the degree of protection Z (3):

$$\gamma = \frac{K_0}{K_\mathrm{i}} \tag{2}$$

$$Z = \frac{(K_0 - K_\mathrm{i})}{K_0} \cdot 100\% \tag{3}$$

where K_0 and K_i are the corrosion rates in the uninhibited acid and in the presence of an inhibitor or a mixture, respectively. The mutual effect of components in the mixture was estimated in terms of the mutual effect factor σ [12]:

$$\sigma = \frac{\gamma_m}{\gamma_1 \cdot \gamma_2} \tag{4}$$

where γ_m, γ_1, and γ_2 are the inhibition coefficients of the mixture and its individual components, respectively.

Polarization measurements were carried out using a PI-50.01 potentiostat (Gomel, Belarus) in a three-electrode temperature controlled cell at a temperature of 25°C. A platinum auxiliary electrode and a silver chloride reference electrode were used. Potentials E were measured with respect to the latter. Polarization curves were measured by varying the potential stepwise from the smaller value of $E=-0.7$ V to the larger value of $E=-0.3$ V at 20 mV steps. Current was recorded after holding E for one minute. Each curve was reproduced in triplicate, then the results were averaged.

Capacitance measurements were conducted using a Z-500 impedance meter (Elins, Russia) in a two-electrode cell in a frequency range of 50 mHz−300 kHz at the corrosion potential. A cylindrical platinum electrode was used as the auxiliary electrode. The degree of coverage of the electrode surface was calculated using the formula:

$$\Theta = \frac{\left(C_0 - C_i\right)}{C_0} \tag{5}$$

where C_0 and C_i is the capacitance of the double electric layer (DEL) in a sulfuric acid solution without and with inhibitors, respectively.

Quantum-chemical calculations were carried out by the Hartree–Fock method in the split-valence basis of Gaussian functions extended with polarization d-functions on heavy atoms 6-311G(d) using the Gaussian09 software [13]. Geometry was optimized without symmetry restrictions; the minima on the potential energy surface were characterized by the absence of imaginary frequencies of calculated normal oscillations.

Results and Discussion

Effect of individual compounds on steel corrosion

Substituted pyrilium perchlorates (PP1 and PP2) are additives of cationic type; sodium diethyldithiocarbamate is anionic; Kaptax, phenylthiourea (PTU), and diphenylthiourea (DPTU) are additives of molecular type.

The adsorption of surface-active compounds on an electrode surface varies significantly depending on the anionic composition of the corrosive medium under study. Let us consider the effect of the explored compounds on the corrosion of low-carbon steel in sulfuric acid.

The protective effect of the studied additives as a function of concentration in the corrosion of low carbon steel in 0.5 M sulfuric acid solution is shown in Figure 1.

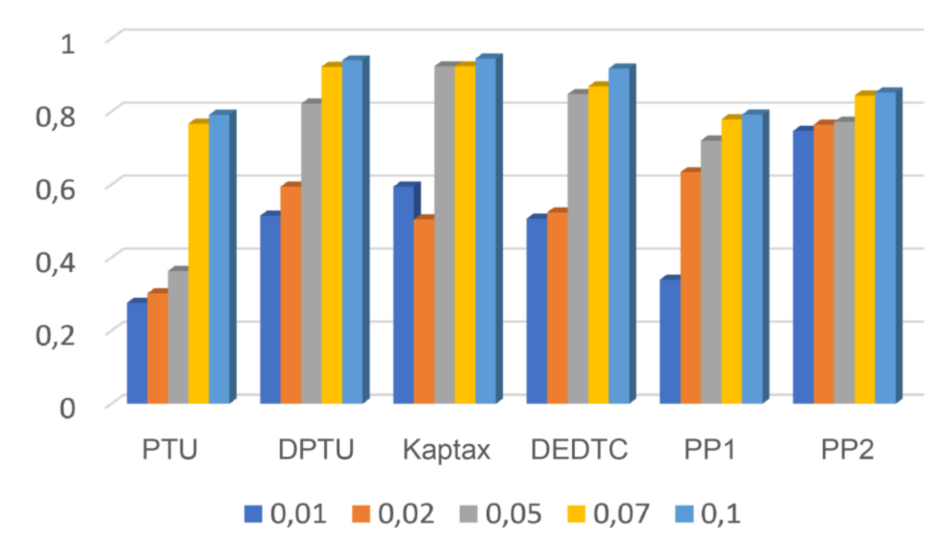


Figure 1. Dependence of the protective effect on the nature and concentration of surface-active compounds, t=25°C, C=0.01–0.1 mmol/L.

With a growth of the concentrations of all additives, the inhibition effect is enhanced. The protective action of acid corrosion inhibitors is caused by their adsorption, blocking of active surface centers, and a change in the effective energy of process activation. The adsorption of the studied compounds on steel surface is described by the Langmuir isotherm (6) with correlation coefficients of 98.6−99.9%.

$$\frac{C}{Z} = C + \frac{1}{K_{\text{ads}}} \tag{6}$$

$$\Delta G_{\text{ads}} = -RT\ln(55.55 \cdot K_{\text{ads}}) \tag{7}$$

where C is the inhibitor concentration (mol/L), Z is the efficiency of the additive, K_{ads} and ΔG_{ads} are a constant and the Gibbs free energy of adsorption, respectively.

The K_{ads} constant and the free energy of adsorption estimated using Equation (7) are presented in Table 2.

Table 2. Inhibitor adsorption energy and effective energy of process activation in the presence of inhibitors in the solution. E^0_{eff} =29.8 kJ/mol.

Parameter	**Values of parameters for inhibitors**					
	PTU	**DPTU**	**Kaptax**	**DEDTC**	**PP1**	**PP2**
$K_{\text{ads}} \cdot 10^5$	5.0	1.1	1.0	1.0	1.0	0.3
$-\Delta G_{\text{ads}}$, kJ/mol	33.8	37.4	37.7	37.7	37.7	40.6
ΔE_{act}, kJ/mol	75.6	33.4	54.7	75.1	73.0	41.8

The values of ΔG_{ads} obtained are indicative of the physical and chemical character of inhibitor adsorption. The value of $\left|\Delta G_{ads}\right|$ only exceeds 40 kJ/mol for the PP2 inhibitor, implying that it is mainly chemisorbed on the steel surface.

In logarithmic coordinates, the plot of inhibition coefficient γ *vs*. C is close to linear, which is an indication that the steel surface is blocked by the inhibitor (see Figure 2).

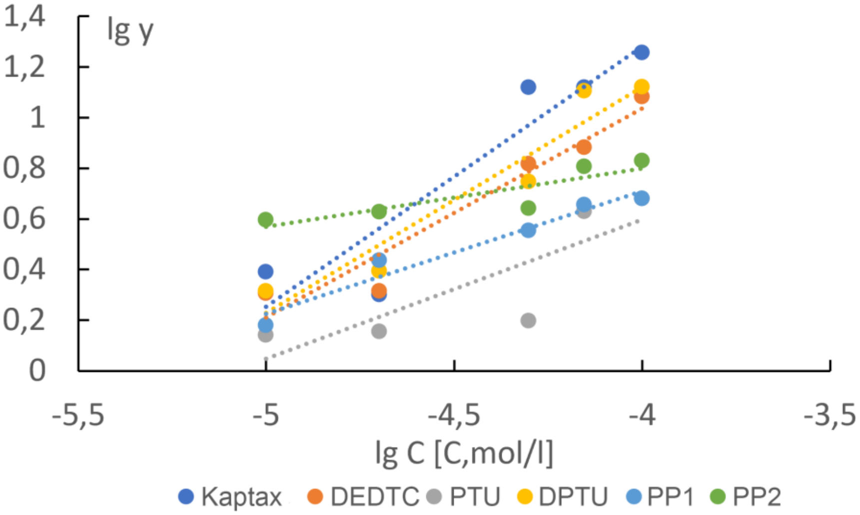


Figure 2. Coefficient of corrosion inhibition in sulfuric acid as a function of concentration of organic compounds.

As the temperature increases, the corrosion rate also increases, while the protective effects of the additives decrease. The effective energies of process activation (E_{eff}) in sulfuric acid with and without inhibitors calculated using the Arrhenius equation are presented in Table 2.

All the additives increase the E_{eff} of the corrosion process; however, the protective effect changes to a different extent (see Figure 3). An increase in temperature by 40°C decreases twofold the degree of protection of the pyrilium perchlorate derivative (PP2), from 71% to 33%. The decrease in the protective effects of thiourea derivatives is 10–20%. The protective effects of PP1, Kaptax, and DEDTC decrease more considerably.

Thus, all studied organic compounds provide an inhibiting effect on steel corrosion at temperatures below 60°C. At high a temperature, thiourea derivatives are efficient.

We have studied the effect of the additives on partial electrode reactions of corrosion, Figure 4.

The inhibitors primarily slow down cathodic release of hydrogen. Additives virtually do not change the polarizability of the cathodic and anodic reactions, as indicated by the close values of Tafel coefficients b_c and b_a. For example, the values of b_c and b_a in the uninhibited acid and in the presence of surface-active compounds are 140±10 and 34±5 mV, respectively. Thiourea derivatives, Kaptax, and PP2 decrease the steel corrosion potential due to which the anodic reaction seems to be stimulated (Table 3).

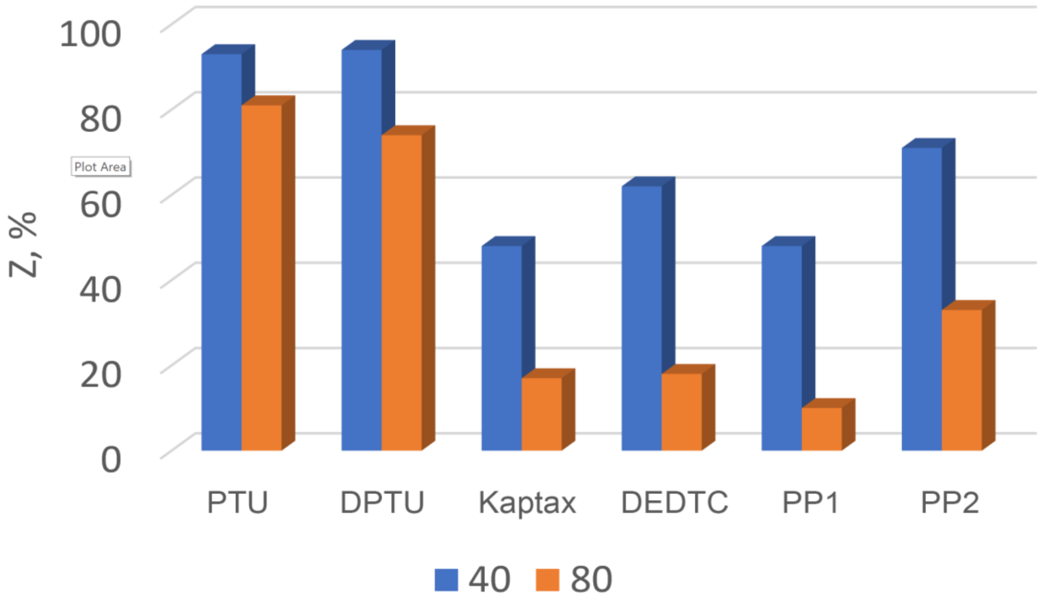


Figure 3. Temperature dependence of the degree of protection provided by the inhibitors.

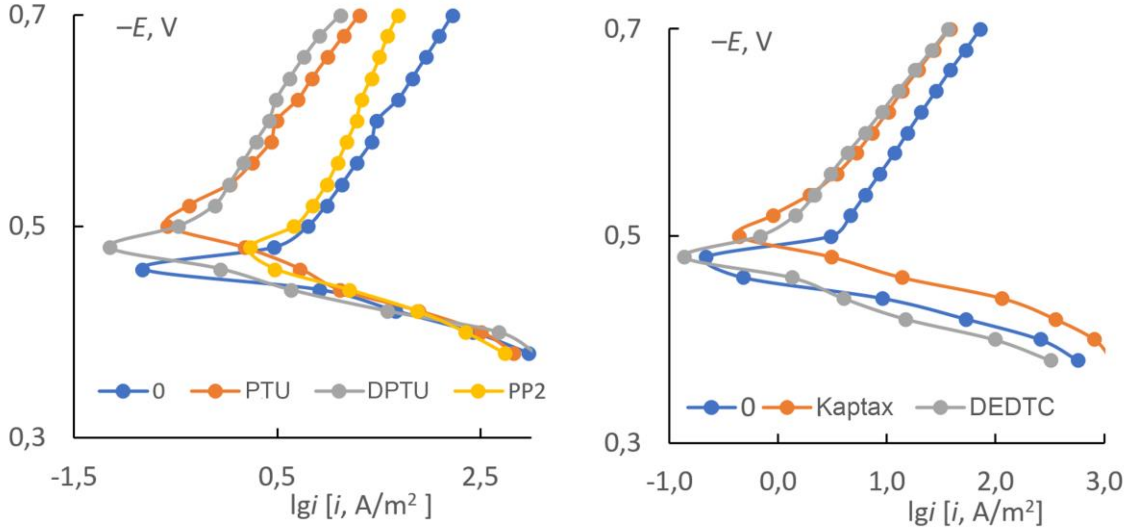


Figure 4. Polarization curves of steel in 0.5 M sulfuric acid without (0) and with additives. C_{SAC}=0.01 mmol/L.

Let us compare the efficiency of the inhibitors under study with the calculated parameters of their molecules. Some calculated characteristics of the inhibitors, including the dipole moment (μ), the energy of the highest occupied and lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}), the total of electron densities on heteroatoms ($\sum_{\mathrm{ED}}$), electronegativity χ ($\chi=(-E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}})/2$), hardness η ($\eta=(-E_{\mathrm{HOMO}}+E_{\mathrm{LUMO}})/2$), and the energy difference between the lowest unoccupied and highest occupied molecular orbitals ($\Delta E=E_{\mathrm{LUMO}}-E_{\mathrm{HOMO}}$) [14, 15] are presented in Table 4.

Table 3. Dependence of the inhibition coefficient of the cathodic and anodic reactions on the potential and the additive nature.

–*E*, mV	**Value of γ for additives**					
	PP2	**PP1**	**PTU**	**DPTU**	**Kaptax**	**DEDTC**
700	3.40	1.27	8.24	12.69	1.91	1.96
640	2.54	1.15	9.69	16.04	2.04	2.24
480	1.73	0.2	1.94	41.15	–	–
420	0.61	1.33	0.59	1.22	0.15	3.59
400	1.19	1.8	0.84	0.56	0.32	2.62
380	1.73	2.04	1.41	0.85	0.48	32.07

Table 4. Calculated characteristics of inhibitors.

Compound	**μ, D**	**$-E_{HOMO}$ (eV)**	**E_{LUMO} (eV)**	**$-\sum_{ED}$, eV**	**χ, eV**	**η, eV**	**Δ*E*, eV**
PP1	4.7999	11.30451499	–3.03354917	1.892	7.169032	4.135483	8.270966
PP2	5.1296	11.08274045	–2.71354075	1.274	6.898141	4.1846	8.3692
PTU	7.224	8.469882616	2.803339032	2.00	2.8335	5.6365	11.27322
DPTU	5.2386	8.202392588	3.032460704	1.895	2.5848	5.526	11.23485
Kaptax	1.2409	8.589613656	2.671362772	0.229	2.9595	5.6305	11.26098
DEDTC	9.801	3.222125556	6.988755228	1.436	–1.8835	5.1055	10.21088

The chemical structures of the compounds under study are significantly different. It is most correct to analyze the dependence between the calculated value and protective efficiency for compounds with similar structure. Let us focus on derivatives of substituted pyrilium perchlorate (group 1) and thiourea (group 2). In both groups, the following patterns are observed: the higher the values of E_{HOMO}, E_{LUMO}, ΔE, $\sum_{ED}$, and η and the smaller the χ value, the stronger the protective effect of a compound. A difference is only observed in the dependence of efficiency on the dipole moment: in substituted pyrilium perchlorates, the protective effect increases as the dipole moment increases, while in thiourea derivatives, the effect decreases. It should be noted that mercaptobenzothiazole, which features the smallest value of μ (Figure 1, Table 4), is the best inhibitor at a 25°C among all the sulfur-containing compounds. Its other calculated characteristics are close to those of thiourea derivatives (Table 4). In the mercaptobenzothiazole and DEDTC pair, the protective effect is the stronger, the larger χ, ΔE, $\sum_{ED}$ and η and the smaller μ, E_{HOMO} and E_{LUMO}.

It is known that larger values of E_{HOMO} and E_{LUMO} facilitate better transfer of electrons to the d-orbital of a metal, while a large negative electron density on heteroatoms facilitates the formation of coordination bonds [16–18]. The relationship between the electron density on the reaction center of the molecule and its protective effect can be analyzed (Figure 1, Table 5).

Table 5. Electron density on molecule atoms.

Compound	**Electron density on atoms, eV**						
	O1	**O2**	**O3**	**F1**	**F2**	**–**	**–**
PP1	–0.451	–0.385	–0.456	–0.299	–0.301	–	
PP2	–0.444	–0.386	–0.444	–	–	–	–
PTU	S	C1	C2	N1	N2	–	–
	–0.373	0.164	0.438	–0.755	–0.872	–	–
DPTU	S	C1	C2	C3	N1	N2	H1, H2
	–0.295	0.255	0.444	0.255	–0.8	–0.8	0.364
Kaptax	S1	S2	C1	C2	C3	N	–
	0.264	–0.051	–0.212	0.262	–0.019	–0.442	–
DEDTC	S1	S2	C1	N	C2	C3	–
	–0.506	–0.506	0.049	–0.424	–0.273	–0.273	–

Calculations show that the electron density on the pyrilium oxygen (O2) nearly does not change if various substituents are introduced. If sulfur should be considered as the reaction center in sulfur-containing compounds, then the density on S2 (Kaptax, DEDTC) and S (PTU, DPTU) atoms should be compared. Based on the value of electron density on the sulfur atom, these compounds can be ordered in the following series of decreasing electron density: Kaptax, DPTU, PTU, and DEDTC. These compounds also contain nitrogen that can perform as an adsorption center. Ordering by decreasing density on nitrogen yields the following series: DEDTC, Kaptax, PTU, and DPTU. The efficiency of phenylthiourea is lower than that of other sulfur-containing compounds whose protective effect differs insignificantly. Thus, no correlation of the inhibitor efficiency with an individual heteroatom is observed.

It should be noted that rather a high correlation, 0.93–0.98 and 0.87–0.98, is observed for the energy difference between E_{LUMO} and E_{HOMO} and the hardness η, respectively, for all the sulfur-containing compounds.

Effect of binary mixtures on steel corrosion

Let us consider the effect of pyrilium perchlorate derivatives with sulfur-containing organic compounds on the corrosion of binary mixtures (Table 6).

Table 6. Dependence of the inhibition coefficient and degree of protection on the nature and concentration of components.

$C\cdot10^5$, mol/L	**Values of γ and Z for mixtures**							
	DEDTC+PP2		**DEDTC+PP1**		**Kaptax +PP2**		**Kaptax +PP1**	
	γ	Z, %	γ	Z, %	γ	Z, %	γ	Z, %
1	3.23	69.08	1.51	33.63	80.78	98.76	6.06	83.5
2	83.08	98.79	1.68	40.47	83.09	98.79	6.82	85.35
5	92.3	98.91	3.29	69.64	116.32	99.14	8.38	88.0
7	223	99.55	6.34	84.23	181.75	99.45	8.49	88.23
	PTU+PP2		PTU+PP1		DPTU+PP2		DPTU+PP1	
1	34.8	97.13	166.6	99.39	5.0	80.0	100.96	99.0
2	22.38	95.53	138.83	99.28	5.66	82.34	158.67	99.36
5	33.41	97.0	151.46	99.34	7.14	85.99	185.11	99.46
7	53.32	98.12	416.5	99.76	9.87	89.86	370.22	99.73

The inhibition coefficients in the presence of inhibitor mixtures in solutions at a temperature of 25°C are larger than those of individual compounds, see Figures 1 and 5. The coefficients of mutual influence of the components are presented in Table 7.

Table 7. Dependence of the coefficient of mutual influence on the nature and concentration of components.

$C\cdot10^5$, mol/L	**Value of σ for mixtures**							
	DEDTC and…		**Kaptax and…**		**PTU and…**		**DPTU and…**	
	PP2	**PP1**	**PP2**	**PP1**	**PP2**	**PP1**	**PP2**	**PP1**
1	0.40	0.06	37.83	0.31	11.88	23.1	12.16	8.36
2	18.32	0.03	30.79	0.17	13.59	11.7	13.36	4.4
5	12.40	0.05	41.69	0.09	19.64	8.84	6.29	3.91
7	37.38	0.08	0.40	0.08	3.23	19.3	0.22	2.8

The mixtures of PP1 with DEDTC or Kaptax exhibit a mutual weakening of efficiency. In the other mixtures, the coefficients of mutual influence are most frequently larger than one and the components mutually enhance each other's protective effect.

If the temperature increases, the protective effect of both the mixtures and individual compounds diminishes; the coefficient of mutual influence of the components also changes (see Tables 8 and 9).

Table 8. Dependence of inhibition coefficients and degree of protection on the composition, concentration of the first component in the mixture, and temperature. Concentration of the second component: C=0.1 mmol/L.

***t*, °C**	**Parameter**	**Values of parameters for the following concentrations of the first component in a mixture, mmol/L**							
		0.01	**0.02**	**0.05**	**0.07**	**0.01**	**0.02**	**0.05**	**0.07**
		PP1+PTU				PP1+DPTU			
40	γ	2.46	28.90	29.25	26.71	35.32	34.71	54.41	51.62
	Z, %	59.41	96.54	96.58	96.26	97.17	97.12	98.16	98.06
60	γ	2.34	6.08	26.99	26.88	22.47	67.66	40.33	17.48
	Z, %	57.27	83.56	96.29	96.28	95.55	98.52	97.52	94.27
80	γ	2.03	4.59	1.98	2.94	1.29	2.82	3.62	8.68
	Z, %	50.84	78.23	49.49	79.79	22.70	64.57	72.39	88.49
		PP1+ Kaptax				PP1+DEDTC			
40	γ	23.77	25.53	24.32	42.20	18.66	43.54	32.23	21.21
	Z, %	95.79	96.08	95.89	97.63	94.64	97.70	96.90	95.28
60	γ	1.05	1.27	1.35	1.91	1.27	2.25	4.04	3.69
	Z, %	4.37	21.47	25.92	47.61	21.48	55.46	75.26	72.92
80	γ	1.54	1.47	1.23	1.36	1.16	1.14	1.50	1.52
	Z, %	35.20	32.1	19.00	26.55	13.63	12.51	33.12	34.37
		PP2+PTU				PP2+DPTU			
40	γ	61.16	70.56	33.16	35.28	98.37	82.84	104.93	149.9
	Z, %	98.36	98.58	96.98	97.17	98.98	98.79	99.04	99.3
60	γ	11.87	9.03	23.75	13.67	48.36	124.34	145	136
	Z, %	91.57	88.92	95.78	92.68	97.93	99.19	99.3	99.26
80	γ	4.71	5.53	25.49	37.8	62.5	38.6	64.02	54.68
	Z, %	78.75	81.93	96.07	97.35	98.4	97.4	98.43	98.17
		PP2+ Kaptax				PP2+DEDTC			
40	γ	29.28	30.65	35.04	67.66	24.67	33.63	31.49	46.84
	Z, %	96.58	96.74	97.14	98.52	95.95	97.03	96.82	96.82
60	γ	7.6	20.58	37.11	37.40	0.98	0.8	1.06	1.2
	Z, %	86.84	95.14	97.31	97.33	–	–	5.85	16.7
80	γ	1	1.15	2.52	35.18	1.17	1.01	1.26	1.97
	Z, %	0	12.86	60.24	97.16	15.11	1.2	20.68	49.39

Table 9. Dependence of the mutual influence coefficient on the nature and concentration of the components and temperature.

$C\cdot10^5$, mol/L	Value of σ for mixtures							
	DEDTC with…		Kaptax with…		PTU with…		DPTU with…	
	PP2	PP1	PP2	PP1	PP2	PP1	PP2	PP1
40°C								
1	6.65	23.55	1.69	12.68	8.54	3.07	31.62	101.2
2	3.31	44.69	1.27	12.82	6.86	29.29	18.53	80.89
5	3.48	30.78	1.64	9.82	3.63	27.58	26.39	118.0
7	0.38	0.64	1.32	7.19	0.30	1.95	0.28	1.64
60°C								
1	1.13	2.39	8.56	1.92	35.99	10.13	62.14	47.28
2	0.09	4.65	2.31	2.58	3.45	29.04	15.88	156.88
5	0.14	5.13	4.81	1.68	15.19	78.98	16.94	57.33
7	0.09	1.60	2.76	0.84	0.43	5.07	8.80	4.51
80°C								
1	0.07	0.64	0.08	1.21	1.57	6.26	59.53	7.60
2	0.05	0.65	0.08	1.18	1.44	14.42	3.71	16.99
5	0.11	0.74	0.31	0.86	12.38	5.44	59.30	18.99
7	0.32	2.17	4.0	1.36	1.10	1.27	0.75	0.40

It should be noted that the mixtures of substituted pyrilium perchlorate with thiourea derivatives preserve their protective properties at elevated temperature as well (Z=48–98%). Mixtures with Kaptax or sodium diethyldithiocarbamate are not efficient at temperatures above 60°C.

The coefficient of mutual influence is determined by the composition, concentration of components, and temperature. The mutual enhancement of the effect of additives at all the temperatures studied persists almost irrespective of the mixture in the case of compositions with thiourea derivatives. The coefficient of mutual influence is also higher than one for a mixture with Kaptax at temperatures below 80°C. The other compositions more often exhibit weakening of the protective properties of components at elevated temperatures (Table 9).

The calculated values of the effective activation energy of the corrosion process in the presence of mixtures in sulfuric acid are displayed in Table 10.

Table 10. Effective activation energies of corrosion depending on the nature and composition of the inhibiting mixture, E^0_{act} =68 kJ/mol.

$C\cdot10^3$, mol/L	Values of E_{act} (kJ/mol) for mixtures							
	PP1 with…				PP2 with…			
	Kaptax	DEDTC	PTU	DPTU	Kaptax	DEDTC	PTU	DPTU
0.01	78.5	79.4	132.4	146.1	152.6	211.7	99.3	65.0
0.02	95.6	98.2	128.3	127.9	134.2	152.9	98.6	97.6
0.05	93.5	85.9	134.8	131.7	124.7	142.7	63.4	66.8
0.07	102.3	86.4	134.4	138.9	41.6	156.5	64.7	68.2

The effect of mixtures on partial electrode reactions is shown in Figures 5 and 6.

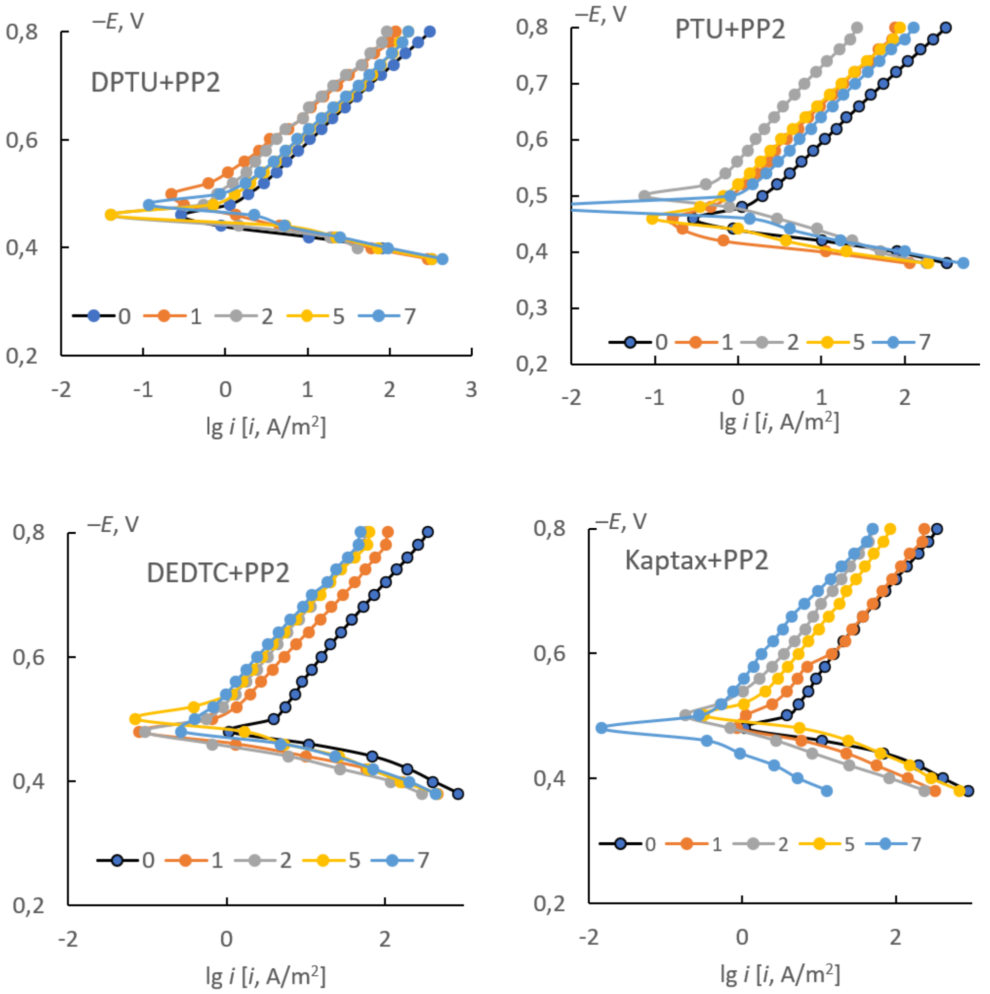


Figure 5. Polarization curves of steel in 0.5 M sulfuric acid without (0) and in the presence of mixtures of PP2 and sulfur-containing organic compounds. C=0.01 mmol/L; C_{PP2}=var, mmol/L: 0.01 (1), 0.02 (2), 0.05 (5), and 0.07 (7).

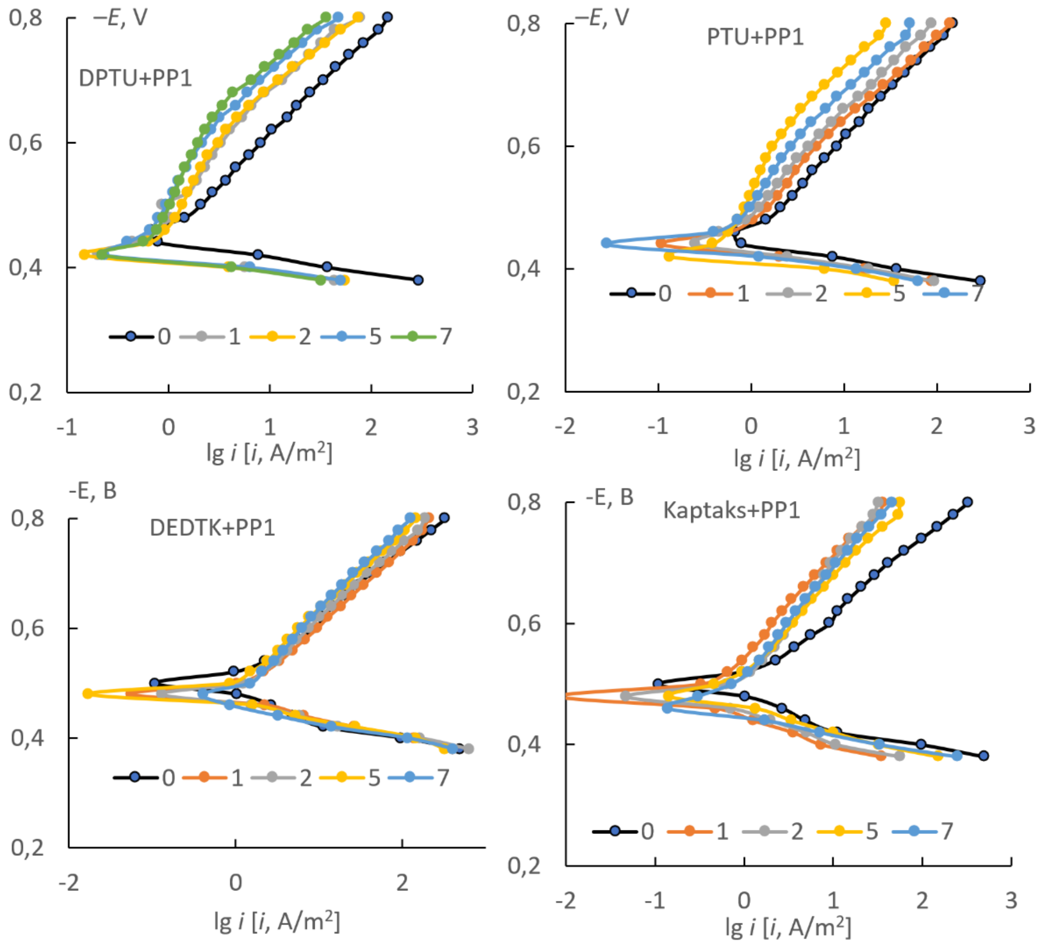


Figure 6. Polarization curves of steel in 0.5 M solution of pure sulfuric acid (0) and in the presence of mixtures of pyrilium perchlorate with DPTU, PTU, DEDTC, and Kaptax. The concentration of sulfur-containing components in the mixture is 0.1 mmol/L; C_{PP1}=var, mmol/L: 0.01 (1), 0.02 (2), 0.05 (5), and 0.07 (7).

Regardless of the concentration of the second component, the mixture slows down both partial electrode reactions of the corrosion process.

Apart from the changes in the process activation energy, acid corrosion inhibitors provide a protective effect by changing the structure of the double electric layer and blocking a fraction of the electrode surface. To determine the coverage of the electrode surface by inhibitors and their mixtures, impedance spectroscopy was used.

The Nyquist plots that characterize the frequency dependence of the real and imaginary impedance components are shown in Figures 7–9.

In the region of medium and high frequencies, the plots have the form of a semicircle, and, if inhibitors or their mixtures are added to the solution and the component concentration in the mixture is varied, its radius is larger than that in pure sulfuric acid. This indicates that the additives and their mixtures manifest an inhibiting effect.

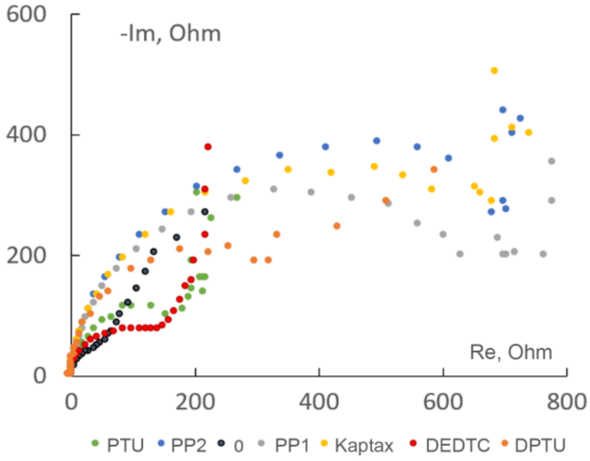


Figure 7. Nyquist plots for a steel electrode in sulfuric-acid solutions in the presence of individual compounds. C=0.1 mmol/L.

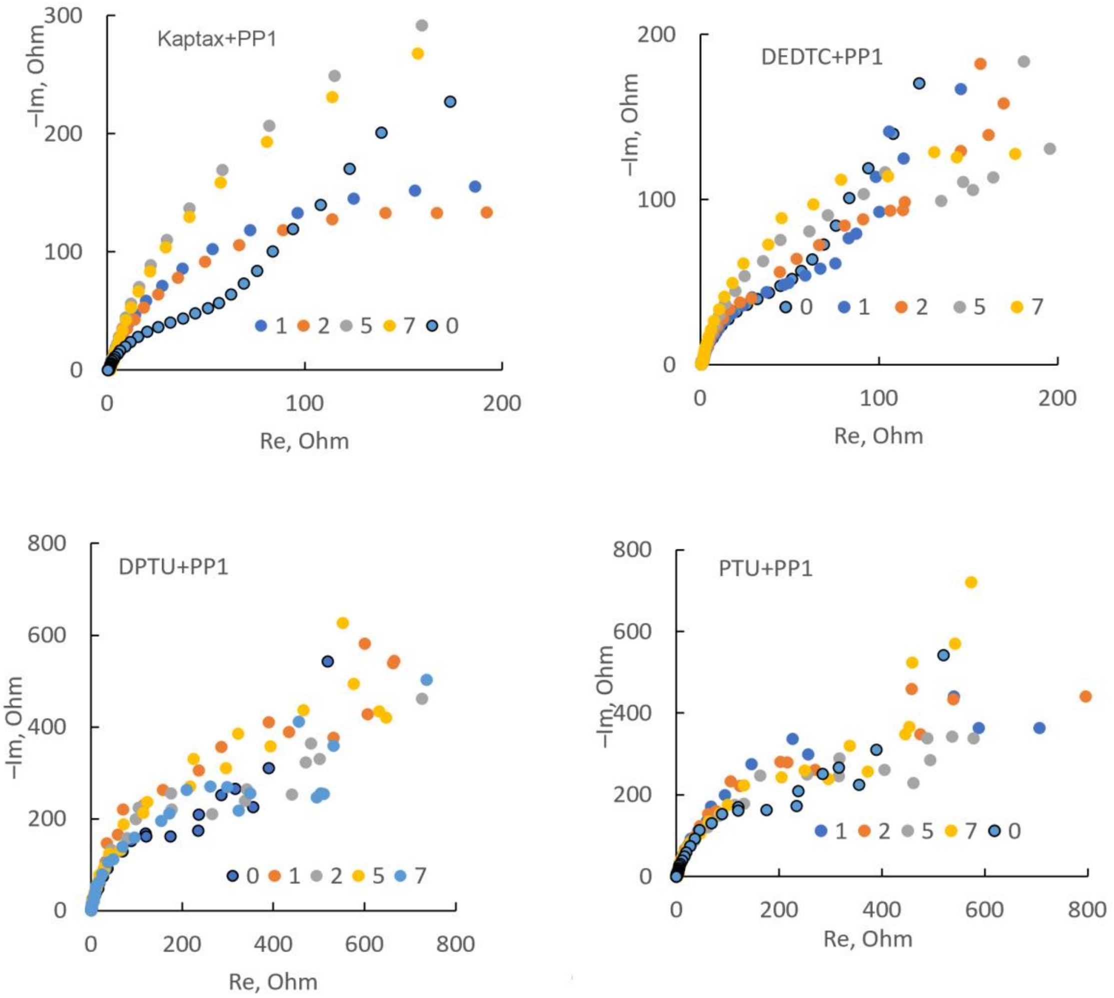


Figure 8. Nyquist plots for a steel electrode in sulfuric acid solutions in the presence of mixtures of compounds. The concentration of the sulfur-containing compound is 0.1 mmol/L; the concentration of PP1 (mmol/L) is 0.01 (1), 0.02 (2), 0.05 (5), and 0.07 (7).

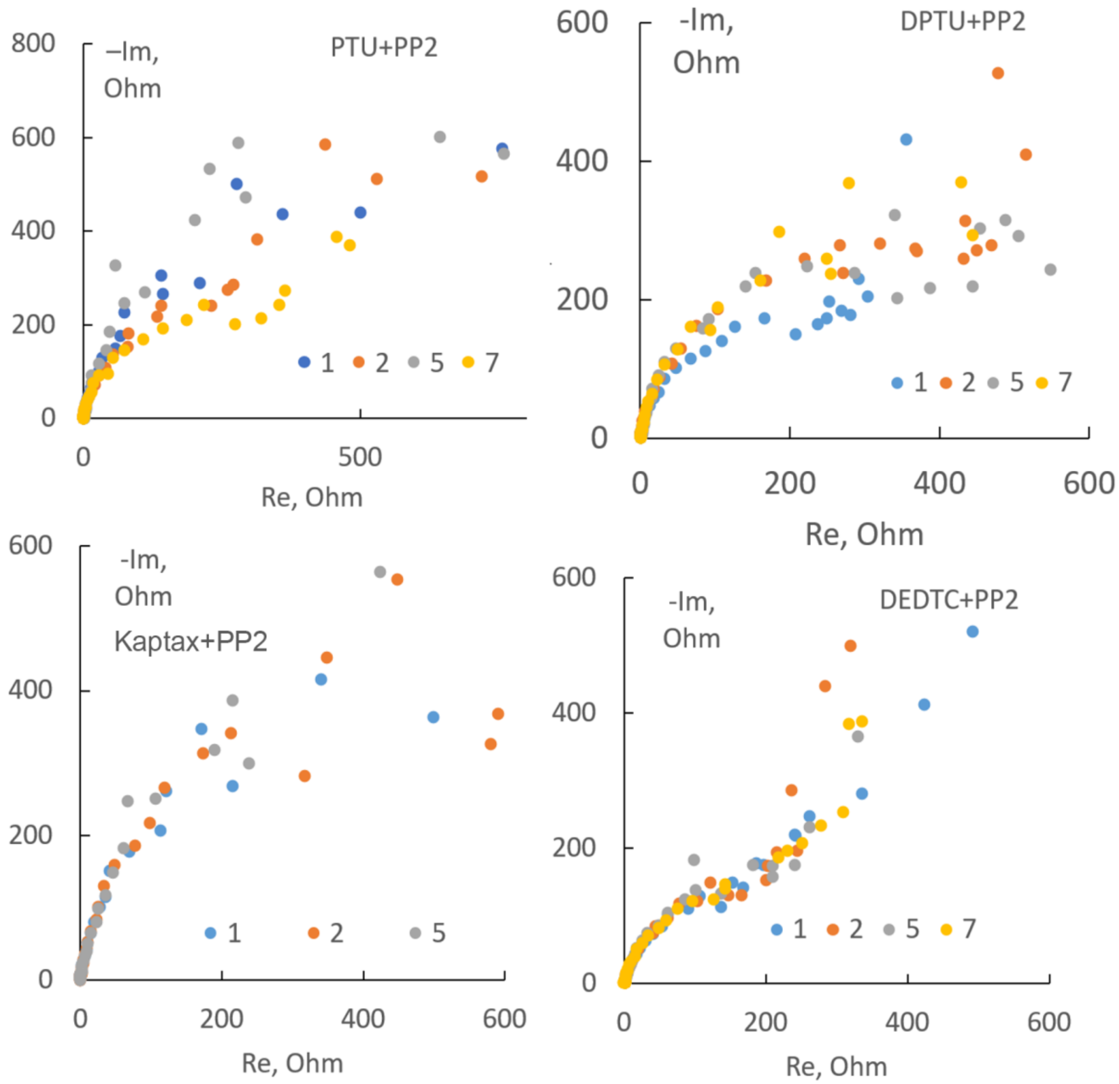
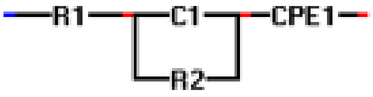


Figure 9. Nyquist plots for a steel electrode in sulfuric-acid solutions in the presence of mixtures of compounds. The concentration of the sulfur-containing compound is 0.1 mmol/L; the concentration of PP2 (mmol/L) is 0.01 (1), 0.02 (2), 0.05 (5), and 0.07 (7).

The plots obtained are satisfactorily simulated by the following equivalent circuit:



(1)

In the equivalent circuit shown above, R_1 is the electrolyte resistance, R_2 is the charge transfer resistance, C is the DEL capacitance, and CPE is the constant phase shift element. The DEL capacitances and the degrees of surface coverage Θ with inhibitors and their mixtures are presented in Table 11.

Table 11. Dependence of the capacitance and the degree of surface coverage on the nature of additives and concentration of one component in the mixture. The capacitance in 0.5 M H_2SO_4 solution is $4.2\cdot10^{-5}$ F. The concentration of individual additives is 0.1 mmol/L.

Additive	**$C\cdot10^5$, F**	**Θ**	**Additive**	**$C\cdot10^5$, F**	**Θ**
PP1	0.37	0.90	Kaptax	1.18	0.48
DEDTC	1.1	0.74	PP2	1.24	0.71
DPTU	1.14	0.73	PTU	1.88	0.55
PP1+DEDTC			PP1+Kaptax		
1*	4.1	0.023	1	1.4	0.67
2	2.18	0.52	2	1.29	0.69
5	2.1	0.53	5	1.6	0.62
7	2	0.52	7	1.8	0.57
PP1+DPTU			PP1+PTU		
1	1.22	0.709	1	1.8	0.57
2	1.73	0.59	2	2.3	0.45
5	1.16	0.72	5	2.3	0.45
7	1.4	0.67	7	1.8	0.57
PP2+DEDTC			PP2+Kaptax		
1	2.5	0.4	1	1.2	0.71
2	2.48	0.4	2	1.2	0.71
5	2.6	0.38	5	1.2	0.71
7	2.6	0.38	7		
PP2+DFTC			PP2+FTC		
1	1.5	0.64	1	1.06	0.74
2	1.24	0.71	2	1.28	0.7
5	1.43	0.67	5	1.26	0.7
7	1.82	0.57	7	1.45	0.67

*Note: Numbers 1, 2, 5, and 7 indicate the concentrations of the second component in the mixture equal to 0.01, 0.02, 0.05, and 0.07 mmol/L.

In the presence of individual organic compounds and their mixtures, in agreement with the expectations, the DEL capacitance is lower than in pure sulfuric acid. In most cases, it changes in a regular manner if the concentration of the mixture components is varied. Sometimes, large capacitance values in mixtures and, consequently, values of the degree of surface coverage with inhibitors that are smaller compared to the pure additives are observed.

It is possible that in the case of joint adsorption of mixture components, effects are exhibited (for example, steric ones) that affect the DEL structure. Nevertheless, the effect of surface blocking works. Inhibitors and their mixtures slow down corrosion by a mixed activation and blocking mechanism.

Conclusions

1. The compounds studied are inhibitors of steel corrosion in sulfuric acid solution.
2. Derivatives of pyrilium perchlorate, phenylthiourea, and diphenylthiourea mutually enhance each other's effects in mixtures regardless of the temperature and composition. Sodium diethyldithiocarbamate and substituted pyrilium perchlorates mostly mutually weaken the protective properties. Mercaptobenzothiazole and pyrilium perchlorates decrease each other's efficiency at temperatures below 80°C.
3. Individual inhibitors are predominantly cathodic-type additives and slow down hydrogen evolution. The mixtures affect both partial electrode reactions of the corrosion process.
4. Components and inhibitor mixtures slow down corrosion by increasing the effective activation energy and blocking the steel surface.

References

1. Ya.G. Avdeev, K.L. Anfilov and Yu.I. Kuznetsov, Effect of nitrogen-containing inhibitors on the corrosion inhibition of low-carbon steel in solutions of mineral acids with various anionic compositions, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 4, 1566–1586. doi: 10.17675/2305-6894-2021-10-4-12
2. Ya.G. Avdeev and M.V. Tyurina, Inhibition of acid corrosion of metals by N-containing six-membered heterocycles: a review, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2017, no. 5, 1–15 (in Russian).
3. P.S. Fakhretdinov, I.Yu. Golubev and R.F. Khamidullin, New imidazolinium compounds based on oxyethylated alkylphenols as acid corrosion inhibitors, *Vestn. Kazan. Tekhnol. Univ.*, 2010, no. 1, 280–287 (in Russian).
4. V.V. Panteleeva, A.B. Shein and I.S. Polkovnikov, Adsorption of some thiadiazole derivatives on low-carbon steel from sulfuric acid solutions, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2019, no. 5, 31–36 (in Russian). doi: 10.31044/1813-7016-2019-0-5-31-36
5. Ya.G. Avdeev, D.S. Kuznetsov and Yu.I. Kuznetsov, Adsorption of IFKhAN-92 corrosion inhibitor on chromium-nickel steel from solutions of mineral acids, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2020, no. 2, 27–32 (in Russian). doi: 10.31044/1813-7016-2020-0-2-27-32
6. Ya.G. Avdeev, Yu.B. Makarychev and D.S. Kuznetsov, Protective aftereffect of IFKhAN-92 inhibitor in corrosion of chromium-nickel steel in sulfuric acid, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2020, no. 12, 23–31 (in Russian). doi: 10.31044/1813-7016-2020-0-12-23-31

7. A.Yu. Luchkin, O.A. Goncharova and N.N. Andreev, Mixed inhibitors. Mutual effect of components, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2021, no. 1, 27–32 (in Russian). doi: 10.31044/1813-7016-2021-0-1-27-32
8. A.G. Berezhnaya, V.V. Chernyavina and I.I. Krotkii, Derivatives of pyrilium perchlorate and berberine as inhibitors of steel corrosion in hydrochloric acid, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2022, no. 2, 37–42 (in Russian). doi: 10.31044/1813-7016-2022-0-2-37-42
9. Ya.G. Avdeev, M.V. Tyurina and Yu.I. Kuznetsov, Protection of low-carbon steel in phosphoric acid solutions by mixtures of a substituted triazole with sulfur-containing compounds, *Int. J. Corros. Scale Inhib.*, 2014, **3**, no. 4, 246–253. doi: 10.17675/2305-6894-2014-3-4-246-253
10. S. Ullah, M.S. Azmi, M. Nadeem, M.A. Bustam, S.A. Shahid, G. Murshid, M.Y. Naz, M. Sagir and M. Mushtaq, The Synergistic Effect of Thiourea and Surfactants on Corrosion Inhibition of Stainless Steel-316 in Hydrochloric Acid, *Adv. Mater. Res.*, 2014, **917**, 28–34. doi: 10.4028/www.scientific.net/AMR.917.28
11. A.G. Berezhnaya, Gh.A.H. Shayea and V.V. Chernyavina, Mixtures of substituted pyridinium perchlorates with sulfur-containing organic compounds as inhibitors of acid corrosion of steel, *Int. J. Corros. Scale Inhib.*, 2017, **6**, no. 4, 372–383. doi: 10.17675/2305-6894-2017-6-4-2
12. V.V. Ekilik and O.V. Chikov, Some diagnostic criteria of the mutual effect of inhibitors of acid corrosion of metals, *Zashch. Met.*, 1991, **27**, no. 1, 72–82 (in Russian).
13. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta Jr, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.
14. G. Bereket, E. Hur and C. Ogretir, Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium, *J. Mol. Struct.: THEOCHEM*, 2002, **578**, no. 1–3, 79–88. doi: 10.1016/S0166-1280(01)00684-4
15. H. Rahmani, F.El Hajjaji, A.El Hallaoui, M. Taleb, Z. Rais, M.El Azzouzi, B. Labriti, K. Ismaly Alaoui and B. Hammouti, Experimental, quantum chemical studies of oxazole derivatives as corrosion inhibitors on mild steel in molar hydrochloric acid medium, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 4, 509–527. doi: 10.17675/2305-6894-2018-7-4-3

16. C. Ogretir, B. Mihci and G. Bereket, Quantum chemical studies of some pyridine derivatives as corrosion inhibitors, *J. Mol. Struct.: THEOCHEM*, 1999, **488**, no. 1–3, 223–231. doi: 10.1016/S0166-1280(99)00033-0
17. G. Moretti, F. Guidi and G. Grion, Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid, *Corros. Sci*., 2004, **46**, no. 2, 387–403. doi: 10.1016/S0010-938X(03)00150-1
18. D. Wang, S. Li, Y. Ying, M. Wang, H. Xiao and Z. Chen, Theoretical and experimental studies of structure and inhibition efficiency of imidazoline derivatives, *Corros. Sci*., 1999, **41**, no. 10, 1911–1919. doi: 10.1016/S0010-938X(99)00027-X

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