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ORGANIC AND PETROCHEMICAL PROCESSES

Inhibitory Activity of Fluorine-containing Quaternary Ammonium Salts Comprising an N-Methylpiperazinyl Moiety

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Abstract—New fluorine-containing quaternary ammonium salts comprising an N-methylpiperazinyl moiety, which exhibited a high inhibiting capacity against hydrochloric acid corrosion of low-carbon steel, were synthesized. The polarization-resistance method was applied to determine the uniform corrosion rate of steel-3 in relation to the structure and concentration of the fluorine-containing substituents in the salts. It was found that the structure of the fluorine-containing moiety of the quaternary ammonium salts does not significantly influence the corrosion processes.

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N-Methylpiperazine is one of the intermediates in production of drugs, including commonly known fluoroquinolone antibiotics, anthelmintics, neuroleptics, etc. [1]. Also, N-methylpiperazine was used for synthesizing compounds having antiarrhythmic [2] and anticancer activity [3]. However, its application is not limited to the synthesis of biologically active compounds. The presence in the molecule of N-methylpiperazine of two heteroatoms suggests its suitability as an independent agent for inhibition of corrosion processes and for synthesis of nitrogen-containing corrosion inhibitors.

Semiempirical quantum chemical calculations [4] showed that, when N-methylpiperazine acts as inhibitor of steel corrosion in acid medium, both its nitrogen atoms initially undergo double protonation. During subsequent physical adsorption on the negatively charged metal surface, the piperazinyl moieties can assume two types of orientation with respect to the substrate, with adsorption occurring via both nitrogen sites or via one of them. In the former case, the piperazinyl framework should adopt a “chair” conformation (flat-lying adsorption). In the latter case, it is attached vertically via the N4 atom (vertical adsorption), because specifically this nitrogen atom has the largest positive charge, as shown by PM3 calculations. In both cases, the orientation of the piperazinyl derivatives is followed by deprotonation.

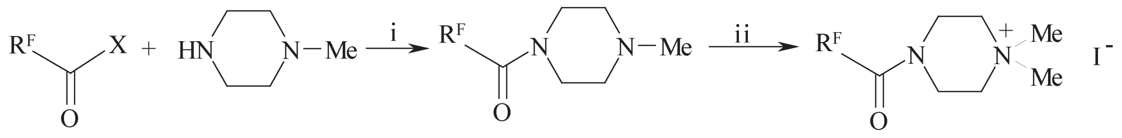
It was shown [5] that medicines, in particular fluoroquinolone antibiotics, hold promise as corrosion inhibitors. Nonconventional use of pharmaceutical products has become the focus of attention of researchers who are looking for corrosion-resistant materials unable of inflicting major environmental damage. Most drugs typically undergo biodegradation under environmental conditions [6–12].

Here, we synthesized fluorine-containing quaternary ammonium salts comprising an N-methylpiperazinyl moiety and examined their inhibition effect against low-carbon steel corrosion in hydrochloric acid.

The choice of fluorinated quaternary ammonium salts (F-QASs) as the subjects of our study was dictated by the following reasons: enhanced, in many cases, solubility of organic and more hydrophobic organofluorine compounds in aqueous media due to the presence of a quaternary nitrogen atom [13, 14], better performance characteristics compared to nonfluorinated analogs [15–17], and the possibility to achieve the desired effect with low-concentration solutions [13].

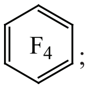
To study the inhibitory effect, reactions of esters of perfluorocarboxylic acids **Ia–Id**, or of 2,3,4,5-tetrafluorobenzoic acid chloride **Ie**, with

N-methylpiperazine were carried to produce amides **IIa–IIe**. The latter were quaternized with methyl iodide to yield highly water-soluble F-QASs **IIIa–IIIe**, which were obtained in quantitative yield:



Ia–Ie **IIa–IIe** **IIIa–IIIe**, 92–97%

X=OEt; R^F = (**a**) CF_3, (**b**) C_3F_7, (**c**) C_4F_9, and (**d**) C_6F_{13}; i: toluene, bp, 2 h; ii: CH_3I, toluene, room temperature; X=Cl; (e)

R^F = 

; i: CH_2Cl_2, room temperature, 2 h; ii: CH_3I, CH_2Cl_2, room temperature.

The uniform corrosion rate K_n of low-carbon steel-3 and the inhibitory activity of compounds **IIIa–IIIe** used in 1×10^{-4} M concentration were studied in a 1 m HCl_{conc} solution at room temperature by the polarization-resistance technique. Four parallel measurements were performed for each K_n value presented in Fig. 1, with the root-mean-square deviation not exceeding 3%. For comparison we used the K_n values obtained in blank runs for steel-3.

The inhibitory activity of quaternary ammonium salts is underlain primarily by the electrostatic interaction between the positively charged nitrogen atom of the ammonium group and the negatively charged electrode [18]. For compounds having complex structures and possessing multiple metal-coordination sites, inhibition follows a more complex mechanism. Possible mechanisms include interaction of unpaired electrons of heteroatoms with vacant *d* orbitals of the metal, formation on the electrode surface of stable chelates which create major corrosion-resistant barriers, and interaction of π electrons (if any) with the metal, as well as all these types of interaction combined [19–21].

As seen from Fig. 1, the highest inhibitory effect is exhibited by F-QAS **IIIa** comprising a trifluoromethyl substituent. Although the available data suggest an increase in hydrophobicity of compounds with increasing length of the fluoroalkyl moiety, it is only in the end portion of the curve for salt **IIId** that there are a number of unstable K_n values, lower compared to F-QAS **IIIa**. The respective values of the degree of protection Z, calculated for F-QASs **IIIa**, **IIIb**, **IIIc**, **IIId**, and **IIIe** by the equation

$$Z = \frac{K_{n1} - K_{n2}}{K_{n1}} \times 100\%,$$

(K_{n1} and K_{n2} are uniform corrosion rates without and with inhibitor, respectively), were 67, 59, 58, 69, and 60 %.

Surprisingly, compound **IIIe** having an additional coordination site with the d-metal surface, π electrons of the aromatic ring, exhibited a lower inhibitory activity. This may be due to the presence in the aromatic moiety of four fluorine atoms whose cumulative inductive effect causes substantial depletion of the π density and does not promote its strong coordination to the electrode surface. Another possible reason is inflexible carbonyl spacer interconnecting the fluoroaromatic and piperazinyl substituents, responsible for weak coordination of π electrons to the d metal.

The general trend revealed for salts **IIIa–IIIe** when used in 1×10^{-4} M concentration is that they cause

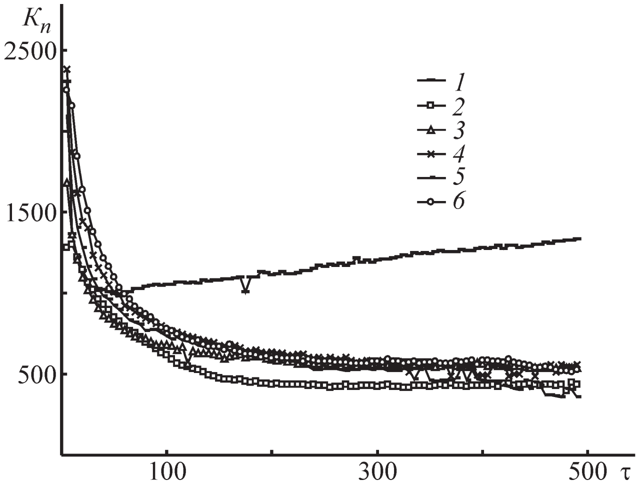


Fig. 1. Uniform corrosion rate K_n, µm year^{-1}, of steel-3 vs. time τ, min, in a 1 M HCl solution at 1×10^{-4} m concentration of salts **IIIa–IIIe.** (*1*) Blank (without salt) run and (*2–6*) runs with (*2*) **IIIa**, (*3*) **IIIb**, (*4*) **IIIc**, (*5*) **IIId**, and (*6*) **IIIe** salts; the same for Fig. 2.

reduction in the hydrochloric acid corrosion rate for low-carbon steel by a factor of 2–4.

To more accurately examine how the structure of the fluoroalkyl (fluoroaromatic) moiety of salts **IIIa–IIIe** affects K_n of low-carbon steel we studied the corrosion processes with the use of **IIIa–IIIe** in 1×10^{-3} M concentration under identical conditions. The results are shown in Fig. 2. The increase in the concentration of F-QASs **IIIa–IIIe** causes their inhibitory activity to increase in all the cases: The parameter *Z* was estimated at 88, 85, and 90% for **IIIa**, **IIIb**, and **IIIc**, respectively, and at 91% for both **IIId** and **IIIe**. The use of salts **IIIa–IIIe** in 1×10^{-3} M concentration causes reduction of the corrosion rate by a factor of 7–11.

The fact that all the profiles demonstrating the time dependence of K_n (Fig. 2, curves *2*–*6*) get close together suggest that, with F-QASs **IIIa–IIIe** as inhibitors, the corrosion processes do not significantly depend on the structure of the fluorine-containing substituent. It becomes evident that the factor deciding the inhibitory properties of compounds **IIIa–IIIe** is physical adsorption of these derivatives on the electrode surface via the positively charged nitrogen atom of the piperazinyl moiety. Considering the data from [4], it can be concluded that F-QASs **IIIa–IIIe** synthesized are prone to vertical adsorption. The effect of the electrode surface protection against corrosive media by hydrophobic fluorine-containing moieties does exist but is not of decisive importance for inhibition of corrosion of steel-3 in hydrochloric acid by compounds **IIIa–IIIe**.

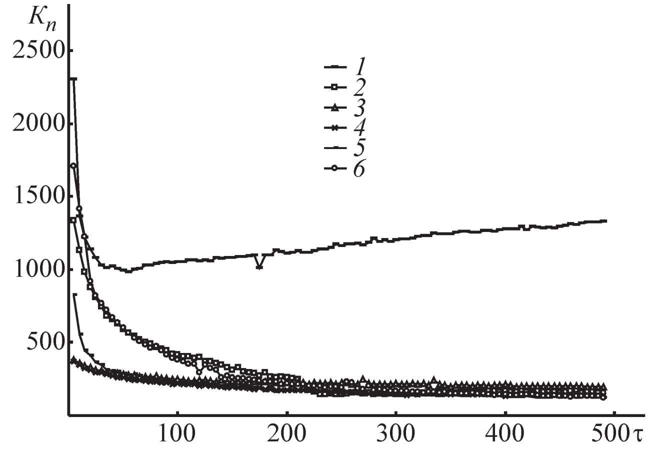


Fig. 2. Uniform corrosion rate K_n, μm year^{-1}, of steel-3 vs. time τ, min, in a 1 m HCl solution at 1×10^{-3} M concentration of salts **IIIa–IIIe**.

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer Spectrum One B spectrophotometer, and NMR spectra, on Bruker DRX-400 spectrometers (^{1}H: 400 MHz, internal reference Me_4Si; ^{19}F: 376 MHz, internal reference C_6F_6). Chemical shifts were measured accurately to within 0.01 ppm, and spin-spin coupling constants, to 0.1 Hz. Elemental analysis was performed on a Perkin Elmer PE 2400 Series II CHNS/O EA 1108.4 elemental analyzer. Melting points were measured in open capillaries on a Stuart SMP3 melting point apparatus.

The uniform corrosion rate of low-carbon steel was examined in a 1 m HCl_{conc} solution using an Expert-004 universal automatic corrosion meter and a two-electrode sensing device, available from Ekoniks Ekspert Limited Liability Company, Moscow. The electrode material was steel-3 [composition, %: Si 0.05–0.15, Mn 0.40–0.65, P no greater than 0.04, Cr no greater than 0.30, S no greater than 0.05]; each electrode area was 0.00078 m^2.

General Procedure for Synthesis of Compounds **IIIa–IIId**

Step 1. To 0.02 mol of compounds **Ia–Id** in 5 ml of toluene, 0.025 mol of *N*-methylpiperazine was added with stirring. The resulting mixture was heated to boiling and kept for 2 h. Low-boiling compounds and excess N-methylpiperazine were distilled off to 140°C. The residues were light yellow viscous liquids, compounds **IIa–IId**, which were used without further purification.

Step 2. Compounds **IIa–IId** were dissolved in 5 ml of toluene, and 0.03 mol of methyl iodide was added with stirring at room temperature. The resulting solids were filtered off and dried for 1 day at room temperature. The products **IIIa–IIId** were obtained in a 92–97% yield.

1,1-Dimethyl-4-(2,2,2-trifluoroacetyl) piperazinium iodide IIIa. White powder, yield 97%, mp 236–237°C (dec.). IR spectrum, ν, cm^{-1}: 1700 (C=O). ^{1}H NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 3.22 s (6H, 2Me), 3.55 t (4H, $2CH_2$, $J = 5.3$ Hz), 3.96 m (4H, $2CH_2$). ^{19}F NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 94.34 s (3F, CF_3). Found, %: C 28.34, H 4.18, F 16.49, N 8.34. $C_8H_{14}F_3IN_2O$. Calculated, %: C 28.42, H 4.17, F 16.86, N 8.29.

1,1-Dimethyl-4-(2,2,3,3,4,4,4-heptafluorobutyryl) piperazinium iodide IIIb. Yellowish powder, yield

94%, mp. 247–249°C (dec). IR spectrum, ν, cm^{-1}: 1697 (C=O). ^{1}H NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 3.22 s (6H, 2Me), 3.55 t (4H, $2CH_2$, *J* = 5.0 Hz), 4.00 m (4H, $2CH_2$). ^{19}F NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 37.26 m (2F, CF_2), 51.04 m (2F, CF_2), 83.57 m (3F, CF_3). Found, %: C 27.36, H 3.18, F 30.12, N 6.34. $C_{10}H_{14}F_7IN_2O$. Calculated, %: C 27.41, H 3.22, F 30.35, N 6.39.

1,1-Dimethyl-4-(2,2,3,3,4,4,5,5,5-nonafluorovaleryl)piperazinium iodide IIIc. White powder, yield 95%, mp 249–251°C (dec.). IR spectrum, ν, cm^{-1}: 1695 (C=O). ^{1}H NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 3.22 s (6H, 2Me), 3.56 t (4H, $2CH_2$, *J* = 4.8 Hz), 4.00 m (4H, $2CH_2$). ^{19}F NMR spectrum: [$(CD_3)_2SO$, δ, ppm]: 38.56 m (2F, CF_2), 40.95 m (2F, CF_2), 51.50 m (2F, CF_2), 82.01 t (3F, CF_3, *J* = 9.8 Hz). Found, %: C 27.02, H 2.84, F 34.93, N 5.69. $C_{11}H_{14}F_9IN_2O$. Calculated, %: C 27.07, H 2.89, F 35.03, N 5.74.

1,1-Dimethyl-4-(2,2,3,3,4,4,5,5,6,6,7,7,7- tridecafluoroenanthyl)piperazinium iodide IIId. Yellow powder, yield 92%, mp 261–262°C (dec.). IR spectrum, ν, cm^{-1}: 1695 (C=O). ^{1}H NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 3.22 s (6H, 2Me), 3.56 t (4H, $2CH_2$, *J* = 5.0 Hz), 4.00 m (4H, $2CH_2$). ^{19}F NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 37.00 m (2F, CF_2), 40.00 m (2F, CF_2), 41.76 m (2F, CF_2), 42.38 m (2F, CF_2), 51.80 m (2F, CF_2), 82.32 m (3F, CF_3, *J* = 9.8 Hz). Found, %: C 26.62, H 2.38, F 41.84, N 4.68. $C_{13}H_{14}F_{13}IN_2O$. Calculated, %: C 26.55, H 2.40, F 41.99, N 4.76.

1,1-Dimethyl-4-(2,3,4,5-tetrafluorobenzoyl) piperazine (IIe). To 0.12 mol of compound Ie in 100 ml of dichloromethane, 0.24 mol of *N*-methylpiperazine was added with stirring. The resulting mixture was kept for 2 h at room temperature, after which the organic layer was separated, washed with a sodium carbonate solution, and distilled under vacuum created by an oil pump, bp 170–175°C (10 Torr). Compound **IIe** was obtained as a yellow liquid, yield 75%. IR spectrum, ν, cm^{-1}: 1700 (C=O). ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 2.33 s (3H, CH_3), 2.38 m (2H, CH_2), 2.48 m (2H, CH_2), 3.34 m (2H, CH_2), 3.80 m (2H, CH_2), 7.67 m (1H, C_6F_4H). ^{19}F NMR spectrum ($CDCl_3$, δ, ppm): 8.83 m (1F), 17.00 m (1F), 25.82 m (1F), 26.40 m (1F). Found, %: C 52.06, H 4.29, N 10.03, F 27.26. $C_{12}H_{12}F_4N_2O$. Calculated, %: C 52.18, H 4.38, N 10.14, F 27.51.

1,1-Dimethyl-4-(2,3,4,5-tetrafluorobenzoyl) piperazinium iodide (IIIe). To a solution of 0.1 mol of compound **IIe** in 50 ml of dichloromethane, 0.02 mol of methyl iodide was added. The resulting solid was filtered off and dried for 1 day at room temperature. The product **IIIe** was obtained as a yellow powder, mp above 233°C (charring), yield 96%. IR spectrum, ν, cm^{-1}: 1698 (C=O). ^{1}H NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 3.19 s (6H, 2Me), 3.40 m (2H, CH_2), 3.51 m (2H, CH_2), 3.69 m (2H, CH_2), 3.98 m (2H, CH_2), 7.52 m (1H, C_6F_4H). ^{19}F NMR spectrum [$(CD_3)_2SO$, δ, ppm]: 8.22 m (2F), 21.74 m (1F), 24.35 m (1F). Found, %: C 37.26, H 3.51, F 18.04, N 6.59. $C_{13}H_{15}F_4IN_2O$. Calculated, %: C 37.34, H 3.62, F 18.17, N 6.70.

CONCLUSIONS

(1) Reactions of esters of perfluorocabroxylic acids, or of 2,3,4,5-tetrafluorobenzoic acid chloride, with N-methylpiperazine were carried out to produce amides whose quaternization with methyl iodide resulted in new water-soluble quaternary ammonium salts.

(2) Examination of the uniform corrosion rate of steel-3 in hydrochloric acid by the polarization-resistance method with the use of quaternary ammonium salts in different concentrations showed that they are effective corrosion inhibitors. When in 1×10^{-4} and 1×10^{-3} M concentrations they cause reduction in the uniform corrosion rate by factors of 2–4 and 7–11, respectively.

(3) It was presumed that the inhibiting action of the compounds examined is not substantially dependent on the structure of the fluorine-containing moiety and is determined by physical adsorption of the positively charged nitrogen atom on the electrode surface.

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