Chem. Chem. Technol., 2017, Vol. 11, No. 3, pp. 314–318

Chemical Technology

QUATERNARY PYRIDINIUM SALTS AS INHIBITORS OF MILD STEEL BIOCORROSION

Iryna Kurmakova[1, *], Olena Bondar[1], Sergey Polevichenko[1], Nataliya Demchenko[1]

https://doi.org/10.23939/chcht11.03.314

Abstract. A number of new quaternary pyridinium salts with amide fragment and aryl substituents have been obtained, demonstrating the inhibition efficiency of 50.0–97.2 % under the biocorrosion of mild steel, induced with sulfate-reducing bacteria of *Desulfovibrio* and *Desulfomicrobium* genera. It has been established that inhibition efficiency of the studied quaternary salts is caused by their effect on microbiological factor.

Keywords: quaternary pyridine salts, biocorrosion, sulphate-reducing bacteria, inhibitor.

1. Introduction

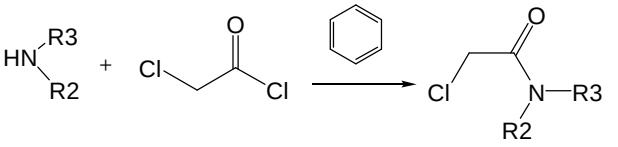
Among pyridine derivatives there are effective inhibitors, which guarantee up to 98 % steel protection against acid, including the hydrogen sulphide, corrosion, and are used as anticorrosive protective means (catapines, I-A, I-B, I-K, I-E, IKONP, IKOMEP, I-25-D) [1]. For some of them, particularly catapine (alkylbenzylpyridinium chloride), biocide effect on the sulfate-reducing bacteria – the main factor of biocorrosion – has been defined [2]. Antimicrobial effect on the named bacteria was also revealed in derivatives of pyridinium salts [3], derivatives of hydrobromide 4-[(4-chlorophenyl)methyl] pyridine [4]. These facts prove that quaternary pyridinium salts have a great potential in the inhibition of steel biocorrosion.

To obtain new quaternary pyridinium salts, possessing biocidal and biocorrosion inhibition characteristics, the previously established "structure–characteristics" rules should be taken into consideration. In [5] it was shown that greater antimicrobial effect can be ensured by the presence of two substituents containing substituted benzene rings in pyridine derivative molecule. As the corrosive aggressiveness of different genera of sulfate-reducing bacteria (from high to almost not expressed) as well as their reaction to the effect of potential biocide inhibitor vary, several cultures should be used in order to define the effectiveness of new compounds [6].

The aim of this paper is to obtain the quaternary pyridinium salts with substitutes containing the structural elements of effective biocides of sulfate-reducing bacteria (amide groups, amides, substituted benzene rings) and to verify their inhibition efficiency to the corrosion caused by bacteria of *Desulfovibrio* and *Desulfomicrobium* genera.

2. Experimental

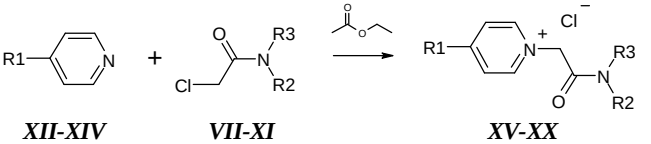
For the synthesis of quaternary pyridinium salts starting materials manufactured by Aldrich, and α-chloroacetanilides (**VII-XI**) obtained by reacting aromatic amines (**I-V**) with chloroacetyl chloride (**VI**) were used:



I-V **VI** **VII-XI**

One mole of chloroacetyl chloride in 300 ml of anhydrous benzene was added dropwise during 1 h to the solution of different anilines (2.21 mol) in 300 ml anhydrous benzene with stirring in three-neck round-bottomed flask. The mixture was stirred for 12 h and the precipitate was filtered and washed with two portions of benzene (25 ml) [7].

The quaternary pyridinium salts (***XV-XX***) were produced by the alkylation of substituted pyridines ***XII-XIV*** with α-chloroacetanilides ***VII-XI*** according to the scheme:



XII-XIV ***VII-XI*** ***XV-XX***

[1] Chernihiv National T.G. Shevchenko Pedagogical University
53, Hetmana Polubotka St., 14013 Chernihiv, Ukraine
[*] *i.kurmakova@gmail.com*

© Kurmakova I., Bondar O., Polevichenko S., Demchenko N., 2017

In a flask 0.1 mol of α-chloroacetanilide (***VII-XI***) was dissolved in ethyl acetate and 0.1 mol of substituted pyridine (***VII-XI***) was added. The mixture was boiled for 5 h under reflux. After cooling for 12 h, precipitate was filtered and the product was dried and crystallized. The solvents used for recrystallization were alcohols (isopropanol, ethanol) [8]. The reaction yield (***XV-XX***) was 85–89 %. Characteristics of compounds (***XV-XX***) are shown in Table 1.

The purity of the compounds (***VII-XI*** and ***XV-XX***) was confirmed with combined gas chromatography (LC/MSD) method on the Agilent 1200 device with mass-spectrometry detector Mass Quad G1956B (Agilent Technologies Inc.) with positive and negative ionization. Column Rapid Resolution HT Cartige 4.6x30 mm, 1.8-Micron, Zorbx SB-C18 (Agilent Zorbx). Chromatographic separation was performed by gradient method with a mixture of water-acetonitrile. The flow rate through the column was 2 ml/min; temperature – 318 K; analysis time – 210 s. Purity was monitored by Diode-arrey G1315B (Agilent Technologies Inc.) multiwave-length diode matrix spectral detector at frequencies of 215 and 254 nm.

The structure of the compounds was confirmed by elemental analysis and NMR ^{1}H spectroscopy (Bruker-300).

4-amino-1-{2-[isopropyl(phenyl)amino]-2-oxoethyl}pyridinium chloride (***XV***): ^{1}NMR(DMSO-d6): δ = 8.3 (s, 2H, NH2); 7.50–7.90 (5H, m, Ph); 7.40 (d, 2H, Py); 6.80 (d, 2H, Py); 4.55 (m, 1H, CH-iPr): 0.95 (d, 6H, 2xCH3-iPr).

1-(2-anilino-2-oxoethyl)-4-(hydrazinocarbonyl) pyridinium chloride (***XVI***): ^{1}NMR (DMSO-d6): δ = 10.50 (S, 1H, NH); 10.50 (s, 1H, NH-Ph); 8.75 (d, 2H, Py); 7.75 (d, 2H, Py); 7.05–7.60 (m, 5H, Ph); 5.60 (s, 2H, NH2); 4.25 (s, 2H, CH2).

1-{2-[(4-ethoxyphenyl)amino]-2-oxoethyl}-4-(hydrazinocarbonyl)pyridinium chloride (***XVII***): ^{1}NMR (DMSO-d6): δ = 10.20 (s, 2H, NH2); 8.75 (d, 2H, Py); 7.75 (d, 2H, Py); 7.50 (d, 2H, Ph); 6.80 (d, 2H, Ph); 4.70 (s, 1H, NH); 4.20 (s, 2H, CH2); 3.95 (m, 2H,-OCH2-CH3); 1.30 (t, 3H,–OCH2–CH3).

1-{2-[(2,4-dimethylphenyl)amino]-2-oxoethyl}-4-(hydrazinocarbonyl)pyridinium chloride (***XVIII***): ^{1}NMR (DMSO-d6): δ = 10.20 (s, 1H, NH-NH2); 9.60 (s,1H, NH); 8,75 (d, 2H, Py); 7.55 (d, 2H, Py); 7.25 (d, 1H, Ph); 7.05 (s, 1H, Ph); 6.90 (d, 1H, Ph); 5.0 (s, 2H, NH-NH2); 4.30 (s,2H,CH2); 2.25 (s, 3H, CH3); 2,15 (s, 3H, CH3).

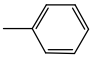
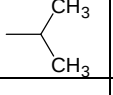
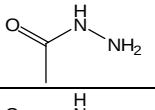
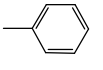
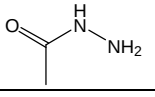
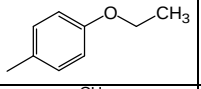
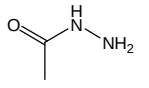
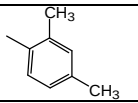
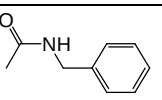
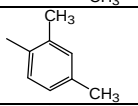
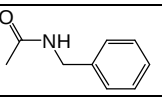
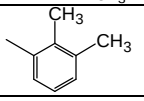
1-{2-[(2,4-dimethylphenyl)amino]-2-oxoethyl}-4-(N-phenylglycil)pyridinium chloride (***XIX***): ^{1}NMR (DMSO-d6): δ = 10.10 (s, 1H, NH); 9.95 (s, 1H, NH); 9.75 (d, 2H, Py); 8.55 (d, 2H, Py); 7.25–7.40 (m, 3H, Ph); 5.75 (s, 2H, NH2); 4.50 (d, 2H, CH2); 2.20 (d, 6H, 2xCH3).

1-{2-[(2,3-dimethylphenyl)amino]-2-oxoethyl}-4-(N-phenylglycil)pyridinium chloride (***XX***): ^{1}NMR (DMSO-d6): δ = 11.00 (s, 1H, NH); 10.40 (s, 1H, NH); 9.30 (m, 2H, Py); 8.55(m, 2H, Py); 7.05–7.45 (m, 5H, Ph); 5.65–5.80 (d, 2H, NH2); 4.55 (d, 2H, CH2); 2.20–2.30 (m, 6H, 2xCH3).

The efficiency of quaternary salts as biocorrosion inhibitors was measured with the help of gravimetric analysis (weight loss method). The mild steel St3ps plates (surface area 0.002 m^2), polished to the 4-5 class of accuracy, were used. Before being placed in the corrosive medium, the steel samples were cleaned with acetone, and weighed with analytical scales accuracy to 0.0001 g.

Table 1

Parameters of quaternary pyridinium salts

Compound	R1	R2	R3	Calculated			Detected		T_m, K
				Mr	*w*(N), %	*w*(Cl), %	*w*(N), %	*w*(Cl), %	
XV	-NH_2			305.80	13.74	11.59	13.16	11.24	592
XVI			-H	306.75	18.26	11.56	18.63	11.33	451
XVII			-H	350.80	15.97	10.11	15.81	11.09	400
XVIII			-H	334.80	16.73	10.59	17.06	10.48	413
XIX			-H	409.91	10.25	8.65	10.05	8.56	408
XX			-H	409.91	10.25	8.65	10.35	8.39	426

Corrosion rate with or without the inhibitors was calculated with the help of the formula:

$$k = \frac{\Delta m}{S \cdot t} \quad (1)$$

where Δm – weight loss, g; S – area, m^2; t – exposure time, h.

Corrosion inhibition coefficient was calculated with the help of the formula (2):

$$g = \frac{k}{k`} \quad (2)$$

where k and k' are the corrosion rates with and without the inhibitor, respectively.

The inhibition efficiency (*IE*, %) was calculated using the following equation:

$$IE = (1 - 1/g) \cdot 100\ \% \quad (3)$$

Model medium Postgate "B" (pH = 7) with sulfate-reducing bacteria of *Desulfovibrio* sp. M.4.1 strain and *Desulfomicrobium* sp. TC 4 strain was used as a testing corrosive medium. Strain *Desulfovibrio* sp. M.4.1. was taken from the corroded iron coating of the subterranean gas pipeline [9]. Strain *Desulfomicrobium* sp. TC 4 (from the corrosion product of brass tubes in water thermal networks) was obtained from the collection of the department of general and soil microbiology and virology, D. K. Zabolotny Institute of Microbiology and Virology. The initial titre of sulfate-reducing bacteria in corrosive medium was 10^9 cell/ml. The samples soaking time was 240 h under 300 K; inhibitor concentration – 0.5 g/l.

The biofilm cells, which appeared on the surface of steel samples during tests, were gathered into the fixed volume (20 ml) of 0.1N phosphate buffer (pH = 7) with the help of ultrasound with the frequency of 25 kHz (30 s) twice with the 60 s interval using UZM-003/n. The resulting swab was used in cultivating and calculating the adhered bacteria cells [10].

On withdrawal of the steel samples, the quantity of free sulfate-reducing bacteria cells was calculated in the culture medium.

The concentration of biogenic hydrogen sulfide was measured with iodometric titration. The degree of influence (*S*, %) of the studied salts on bacteria sulfate reduction was calculated using the formula:

$$S = \frac{C - C'}{C} \cdot 100\ \% \quad (4)$$

where C and C' are the average hydrogen sulphide concentrations with and without the inhibitor, respectively, mg/l.

Statistical analysis of experimental data (the corrosion rate) for the reliability level of 95 % was conducted with the help of Microsoft Excel. The experiment was conducted three times. Linear regressive analysis was performed to define the approximation coefficient and the regression equation.

3. Results and Discussion

It was revealed that synthesized quaternary pyridinium salts have different effect on the rate of steel St3ps biocorrosion, caused by sulfate-reducing bacteria of *Desulfovibrio* sp. M.4.1 strain and *Desulfomicrobium* sp. TC 4 strain (Table 2). The most effective inhibitor of the corrosion, caused by *Desulfovibrio* sp. M-4.1, in Postgate "B" medium turned out to be compound ***XX***, containing 2,3-methyl-phenyl substituent and *N*-benzylcarboxamide fragment. After steel samples soaking in the corrosive medium with this inhibitor, there was no visible sulfide biofilm on their surface. Effectiveness of inhibitor ***XX*** results from the substantial effect on metabolic activity of sulfate-reducing bacteria, causing the reduction of biogenic hydrogen sulfide concentration by 13.3 times compared to the control test and the decrease of the bacteria number in suspension and biofilm by 7 orders. The substantial effect of compound ***XX*** on the number of biofilm bacteria, which are less sensitive to the biocides and more active, compared to the microorganisms of plankton growth forms, is also important for the corrosion inhibition.

The comparatively high protection rate was established for the compound ***XVIII***, which differs from substance ***XX*** by the position of methyl radicals in benzene ring and the presence of hydrazine carbonyl fragment, and compound ***XV***, containing amides in the position 4 of pyridine ring, unsubstituted phenyl and isopropyl substituents. The inhibition effect of these compounds is also due to their effect on the biological factor, which prevails under the biocorrosion [11]. Apart from this, compound ***XVIII*** guarantees the decrease of the number of bacteria in corrosive solution and biofilm up to 10^4, reducing their metabolic activity by 8.18 times. At the same time, compound ***XV*** has a significant effect on the number of bacteria in biofilm (reduction by 6 orders) but has almost no effect on the bacteria in the corrosive solution (free bacteria). The compound ***XIX***, which differs from substance ***XX*** only by the position of 2-methyl substituents in benzene rings, increases the corrosion rate by 1.25 times, as it has almost no effect on microbiological parameters. The correlation between the methyl substituents position and the antimicrobial and inhibitory effect of the compounds agrees with the previously obtained data from the research on the use of tryazoloazepine bromides as inhibitor-biocides [12].

Compounds ***XVI*** and ***XVII***, containing hydrazine carbonyl fragment similar to compound ***XVIII***, showed comparatively low effectiveness, reducing the number of bacteria by only 1-2 orders and reducing the biogenic hydrogen sulfide concentration by 1.7 and 1.3 times, respectively.

Table 2

The effectiveness of quaternary pyridinium salts in inhibiting biocorrosion steel St3ps

Compound	Corrosion rate ($k \cdot 10^3$), g/(m^2·h)	Corrosion inhibition coefficient (γ)	Inhibition efficiency (*IE*), %	Concentration of hydrogen sulfide (*C*), mg/l	Quantity of sulfate-reducing bacteria	
					In corrosive solution, cell/ml	In biofilm, cell/cm^2
strain *Desulfovibrio sp.* M-4.1						
–	35.00±2.12	–	–	319±14	10^9	10^8
XV	2.24±0.18	15.6	93.6	163±7	10^8	10^2
XVI	17.41±1.22	2.0	50.0	188±8	10^7	10^7
XVII	15.98±0.45	2.2	54.6	253±8	10^7	10^7
XVIII	1.98±0.12	17.7	94.4	39±2	10^4	10^4
XIX	43.75±0.38	0.80	–	321±12	10^8	10^7
XX	0.99±0.05	35.2	97.2	24±1	10^2	10^1
strain *Desulfomicrobium sp.* TC4						
–	17.48±0.97	–	–	308±12	10^9	10^8
XV	5.85±0.35	2.9	65.5	296±10	10^8	10^4
XVI	22.41±1.65	0.78	-	146±9	10^8	10^7
XVII	8.69±0.40	2.0	50.0	19±1	10^7	10^6
XVIII	3.35±0.12	5.1	80.4	404±19	10^8	10^6
XIX	3.54±0.17	4.9	79.6	389±14	10^8	10^6
XX	5.50±0.24	3.2	68.8	326±10	10^8	10^3

The correlation between the logarithm of inhibition coefficient of mild steel biocorrosion caused by *Desulfovibrio sp.* M-4.1 and the effect rate on bacterial sulfatereduction (Fig.) has been established. The correlation equation: lg$g$ = 0.0165S – 0.1283. The approximation coefficient value R^2 = 0.95 indicates the high degree of linear dependence, which should be taken into consideration in the future development of new quaternary pyridinium salts for inhibiting the corrosion, induced by the named bacteria strain.

The studied quaternary salts have less effect on steel St3ps biocorrosion, caused by the bacteria *Desulfomicrobium sp.* TC4, which are less aggressive (the steel corrosion rate is 2.9 times less) compared to the *Desulfovibrio sp.* M-4.1 strain. This effect is due to the higher resistance of *Desulfomicrobium sp.* TC4 to quaternary pyridinium salts and somewhat agrees with research data of the named strains [13].

Compound ***XX*** turns out to have the biggest effect on the number of sulphate reducing bacteria in the biofilm formed with *Desulfomicrobium sp.* TC4. With compound ***XX*** the number of bacteria decreases by 5 orders. However, this inhibitor has almost no effect on the number of free bacteria. The high sulphate reducing activity of the microorganisms causes a significant (a little higher than the control test) hydrogen sulphide concentration in the corrosive medium, which explains low compound ***XX*** inhibition efficiency at 68.8 %. Compound ***XV***, the inhibition efficiency of which is 65.5 %, similarly to compound ***XX***, has greater effect on the number of biofilm bacteria (decreases by 4 orders). At the same time, the titre of sulfate-reducing bacteria in the corrosive solution and biogenic hydrogen sulphide concentration are still high.

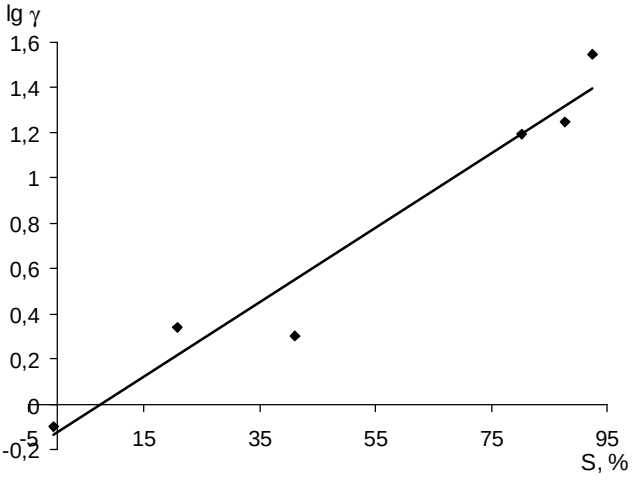


Fig. Correlation between the inhibition coefficient logarithm (lg$g$) and the effect rate on the sulfate reduction (S) of *Desulfovibrio sp.* M-4.1 strain bacteria

Compound ***XVIII*** with 2,4-methyl-phenyl substituent and hydrazine carbonyl fragment proved to be the most effective (protecting the steel by 80.3 %). This

quaternary salt increases the bacteria sulfate-reducing activity, leading to the accumulation of hydrogen sulphide in the corrosive solution. The hydrogen sulphide concentration exceeds the control test by 1.3 times. The dense black sulphide biofilm is formed on the steel samples surface. Such biofilm is known to guarantee the inhibition efficiency, although with the increase in the time of exposure may enhance corrosion processes [14].

Compound ***XVII*** inhibits the sulphate reducing activity of *Desulfomicrobium sp.* TC4 strain. However, it has little effect on the number of biofilm and plankton bacteria, leading to its low (50.0 %) inhibition efficiency. Compound ***XVI*** has a completely opposite effect, enhancing the steel St3ps biocorrosion.

A correlation between the compounds' effect on the microbiological factor and the steel protection rate provided by them, can be stated for *Desulfomicrobium sp.* TC4 as well as for *Desulfovibrio sp.* M-4.1. However, there is no correlation between microbiological and corrosive parameters.

According to the obtained data, the studied quaternary pyridinium salts are more effective for the protection of the steel against biocorrosion in the medium with bacteria of *Desulfovibrio* genus.

4. Conclusions

Quaternary pyridinium salts with the amide fragment and aryl substituents may ensure the protection of mild steel St3ps by 50.0–97.3 % under the microbial corrosion, caused by the sulfate-reducing bacteria of *Desulfovibrio* and *Desulfomicrobium* genera. Their inhibition efficiency is caused by the effect on microbiological factor. The most effective inhibitor in the medium with bacteria of *Desulfovibrio* genus is 1-{2-[(2,3-dimethylphenyl)amino]-2-oxoethyl}-4-(N-phenylglycil)pyridinium chloride, which with the concentration 0.5 g/l shows the inhibition rate of 97.3 % and can be used for the development of new anticorrosive materials for the protection of subterranean metal constructions.

Acknowledgements

The authors are grateful to Prof. A.M. Demchenko for the advice on the synthesis of quaternary pyridinium salts.

References

[1] Pogrebova I.: Ingibitory Korozii Metaliv. Hai-Tek Pres, Kyiv 2012.
[2] Purish L., Kozlova I., Pogrebova I.: Praktika Protivokorrozionnoi Zaschity, 2013, **67**, 18.
[3] Pogrebova I., Purish L., Krasnopir T. *et al.*: Fizyko-Khim. Mekhanika Mater., 2002, **3**, 708.
[4] Demchenko N., Kurmakova I., Tretyak O.: Mikrobiol. Zh., 2007, **69**, 26.
[5] Agaev N.: Fizyko-Khim. Mekhanika Mater., 2000, **1**, 572.
[6] Enning D., Garrelfs J.: Appl. Environ. Microbiol., 2014, **80**, 1226.
[7] Aroyan A., Babayan N., Vartanyan S. *et al.*: Sintezy Heterotsyklycheskykh Soedineniy. Izd-vo AN ArmSSR, Erevan 1972.
[8] Abuhaie C., Ghinet A., Farce A. *et al*: Eur. J. Med. Chem., 2013, **59**, 101. https://doi.org/10.1016/j.ejmech.2012.11.008
[9] Demchenko N., Kurmakova I., Tretyak O.: Microbiol. i Biotekhnolog., 2013, **4**, 90.
[10] Egorov N.: Rukovodstvo k Prakticheskim Zanyatiyam po Microbiologii. Izd-vo Mosk. Univ., Moskva 1983.
[11] Kozlova I., Radchenko O., Stepura L. *et al.*: Heokhimichna Diyalnist Mikroorganizmiv ta ii Prykladni Aspekty. Naukova dumka, Kyiv 2008.
[12] Prihodko S., Kurmakova I., Demchenko N., Tretyak O.: Fizyko-Khim. Mekhanika Mater. 2006, **2**, 919.
[13] Demchenko N., Kurmakova I., Tretyak O.: Visnyk Kharkiv. Nats. Univ. im. V. N. Karazina, 2015, **1153**, 131.
[14] Ryazanov A., Vigdorovich V., Zavershinskij V.: Vestnik Tambovskogo Univ., 2003, **5**, 821.

Received: July 07, 2016 / Revised: November 23, 2016 / Accepted: January 22, 2017

ЧЕТВЕРТИННІ СОЛІ ПІРИДИНІЮ ЯК ІНГІБІТОРИ МІКРОБНОЇ КОРОЗІЇ НИЗЬКОКАРБОНОВОЇ СТАЛІ

Анотація. *Одержано ряд нових четвертинних солей піридинію з амідним фрагментом та арильними замісниками, які проявляють захисну дію 50,0–97,2 % при мікробній корозії низькокарбонової сталі, індукованої сульфат-відновлювальними бактеріями родів Desulfovibrio та Desulfomicrobium. Встановлено, що інгібіторні властивості досліджених четвертинних солей зумовлені їх впливом на мікробіологічний чинник.*

Ключові слова: *четвертинні солі піридинію, біокорозія, сульфат-відновлювальні бактерії, інгібітори.*