

Quaternary ammonium bromides as mild steel corrosion inhibitors in acid media

A. K. Popova*¹, A. A. Vasilev², N. Ivanova¹

¹Department of Physical Chemistry, University of Chemical Technology and Metallurgy, 8 “Kl. Ohridski” blvd., 1756 Sofia, Bulgaria

²Department of Pharmaceutical and Applied Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1 “James Baucher” blvd., 1126 Sofia, Bulgaria

Received December 16, 2019; Accepted January 22, 2020

Three quaternary ammonium bromides are used as inhibitors of mild steel corrosion in 1 M. Their behavior is studied with the application of gravimetric and potentiodynamic voltammetry methods. Additional gravimetric experiments are carried in 1 M aiming a comparison of the protective properties observed. Data referring to the adsorption of the compounds studied is obtained. It is found that it is well described by Frumkin adsorption isotherm. The information summarized leads to the conclusion that the inhibitive properties of the bromides investigated depend on their concentration and molecular structure.

Keywords: mild steel, acid corrosion, acid inhibition, adsorption

INTRODUCTION

Corrosion is a thermodynamically determined spontaneous process which proceeds most often following an electrochemical mechanism. It is based on two partial reactions – an oxidation of the metal and a reduction of the oxidizing agent [1-3].

The enormous material losses in the field of industry caused by corrosion make the latter a significant economic problem. That is why the elaboration of methods for corrosion protection is a research trend of great priority.

The use of corrosion inhibitors is an approach of great importance [4-6]. The efficiency of the compounds used as inhibitors depends directly on their molecular structure and ability to form a protective layer on the metal surface. In an acid medium the inhibition is exercised by a layer of the inhibitor's adsorbed molecules. The elucidation of a connection between the protective properties and the molecular structure of the organic substances used as inhibitors in aqueous acid solutions is of a profound interest [7-30].

Our former investigation show that the inhibitor activity depends essentially on the area of the adsorbed molecule and the spatial disposition of its substituents [31-34]. The effect of the electronic structure becomes evident when the behavior of inhibitors of approximately identical molecular area and planar structure is comparatively considered [33].

It is found that compounds of the group of the quaternary ammonium salts provide very good

protective properties [35-49]. This determines our interest and focus on them. The present communication refers to the continued investigation of the inhibiting properties of quaternary ammonium bromides in case of mild steel corrosion in 1 M and 1 M [34,50]. The molecular structure of the substances studied is chosen to outline the effect of the adsorbed species area through comparing the behavior of molecules of a different size and that of the electronic structure by juxtaposing compounds discriminated by the presence of S or O atom (Table 1). The compounds used in this investigation are specifically synthesized and studied for the first time as inhibitors in correspondence with the views pointed above [51].

EXPERIMENTAL

The mild steel used had the following chemical composition (wt%): 0.16 C, 0.35 Mn, 0.016 Si, 0.01 P, 0.029 S, 0.06 Cr, 0.10 Cu and Fe to balance the content.

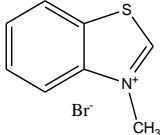
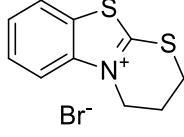
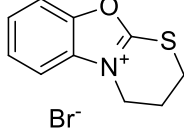
All compounds investigated (Table 1) were purified to an analytical purity grade confirmed by an elemental analysis and ¹H-NMR [51]. 1 M HCl and 1 M H₂SO₄ solutions were prepared using 35% HCl and 98% H₂SO₄ (pure for analysis) and doubly distilled water.

Two classical techniques were used to determine the corrosion inhibitor characteristics of the quaternary ammonium bromides – gravimetry and potentiodynamic voltammetry.

* To whom all correspondence should be sent.

E-mail: apopova@uctm.edu

Table 1. Investigated quaternary ammonium salts as inhibitors

Compounds	Structural formulae	Abbreviation	Molar mass
3-Methylbenzo[d]thiazol-3-ium bromide		MTB	230.1
3,4-Dihydro-2H-benzo[4,5]thiazolo[2,3-b][1,3]thiazin-5-ium bromide		SS	288.9
3,4-Dihydro-2H-benzo[4,5]oxazolo[2,3-b][1,3]thiazin-5-ium bromide		OS	272.2

The gravimetric measurements were carried out at definite time intervals of 24h [34, 52] at a room temperature ($20 \pm 2^\circ\text{C}$) using an analytical balance (precision of ± 0.1 mg). The specimens of an area of 11.3 cm^2 were of a round shape to avoid edges effects attributed to high-speed corrosion proceeding. The preliminary treatment included pickling in a solution containing concentrated HNO_3 and H_2SO_4 at a volume ratio of 2:1, washing with distilled water and an ethanol-ether mixture. Three specimens were immersed simultaneously in every beaker containing 250 mL of the test solution.

The potentiodynamic polarization experiments were carried out in a conventional three-compartment electrochemical cell. A mild steel cylinder pressed into a Teflon holder served as a working electrode (WER). Its working area of 0.5 cm^2 remained precisely fixed. A saturated calomel electrode (SCE) connected through a salt bridge was used as a reference electrode, while platinum sheet acted as counter electrode. Prior to each experiment the WE was wet abraded with 600-grade emery paper, rinsed with distilled water and an ethanol-ether mixture. Then it was inserted immediately into the glass cell which contained 250 mL of the test solution.

EG&G Instruments PAR model 273 potentiostat monitored by an IBM personal computer via a GPIB-IIA interface and M342 software were used to run the tests as well as to collect and treat the experimental data.

The polarization curves were recorded from ca -250 mV to +130 mV vs. the measured corrosion potential E_{corr} with a scan rate of 0.2 mV/s starting one minute after the immersion of the WE in the test solution. The anodic (b_a) and cathodic (b_c)

Tafel constants, the corrosion potential (E_{corr}) and the corrosion current density (j_{corr}) were determined using PARCalc342 data analysis technique (based on the Stern-Geary kinetics equation [53]). The polarization resistance R_p was evaluated on the ground of the same polarization curves but using only the range from ± 10 mV vs. E_{corr} .

All plots and calculated parameters were mean values of at least five independent experiments. Standard deviations were also reported.

The inhibitor efficiency IE (%) was calculated from the gravimetric and potentiodynamic measurements using the relations:

$$IE(\%) = \frac{w_0 - w_i}{w_0} \times 100 \quad (1)$$

$$IE(\%) = \frac{j_{\text{corr},0} - j_{\text{corr},i}}{j_{\text{corr},0}} \times 100, \quad (2)$$

where w_0 and w_1 in $\text{g/m}^2\text{h}$ are the average corrosion rates in absence and presence of an inhibitor, while $j_{\text{corr},0}$ and $j_{\text{corr},i}$ are the corresponding corrosion current densities.

RESULTS AND DISCUSSION

3.1. Inhibiting efficiency

3.1.1. Gravimetric tests

The quaternary ammonium salts are studied in 1M HCl and 1M H_2SO_4 solutions of a wide concentration range. The highest possible concentration value is limited by the plateau reached in the corresponding concentration dependence of the inhibiting efficiency or the compound solubility (10^{-3} M for SS and 5×10^{-4} M in case of SO). The mean values of the corrosion rate, w ($\text{g/m}^2\text{h}$), and that the corresponding inhibiting

efficiency, IE (%), evaluated in accordance with Eq. (1), are determined for each concentration studied. Fig. 1 illustrates the results obtained in 1 M HCl medium, while Fig. 2 – those in 1 M H_2SO_4 solution. It is worth noting that the value of the surface coverage degree, θ , is plotted on the ordinate axis assuming that $IE(\%) = \theta \times 100$. The same data is used in adsorption characteristics determination.

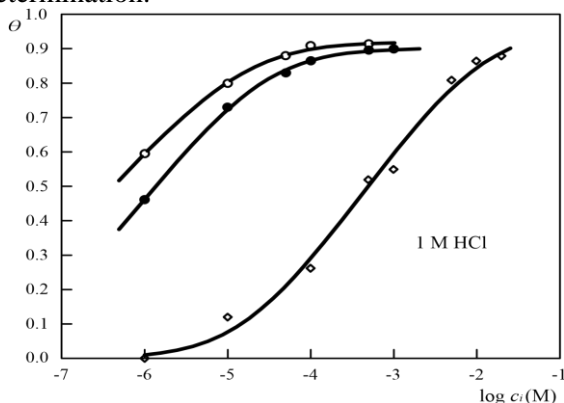


Fig.1. Inhibition efficiency and adsorption isotherms of quaternary ammonium bromides in 1 M HCl - experimental gravimetric data referring to OS (○), SS (●) and MTB (◇) and graphs presenting the adsorption isotherms evaluated.

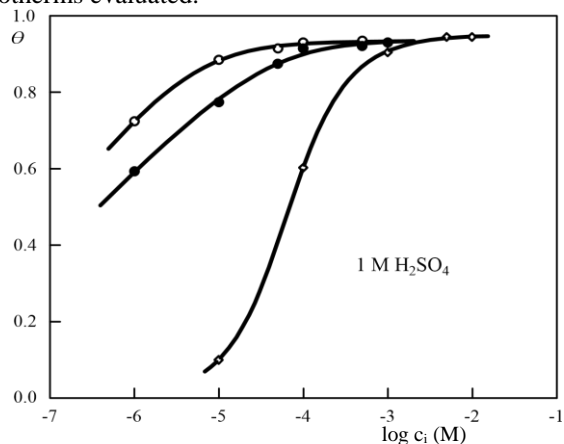


Fig 2. Inhibition efficiency and adsorption isotherms of quaternary ammonium bromides in 1 M H_2SO_4 - experimental gravimetric data referring to OS (○), SS (●) and MTB (◇) and graphs presenting the adsorption isotherms evaluated.

The figures pointed above show that the efficiency of the compounds studied depends on their concentration. It is seen that the protective effect increases initially with the increase of the concentration, c_i . It changes slightly upon reaching a definite concentration value accepted as an optimal one. The latter has a different characteristic value for each inhibitor. The difference in the inhibiting properties of the three compounds is

obviously connected with the difference in their molecular structure. It is more vividly expressed at low and medium concentration values.

The comparison of the inhibitors in 1 M HCl in view of the maximal efficiency reached leads to the following line:

OS (91.5%) \approx SS (90.0%) > MTB (88.0%).

At a concentration of 1×10^{-4} M the line changes to:

OS (91.0%) > SS (86.5%) > MTB (26.0%).

The same line is obtained at lower inhibitor concentrations as well.

The inhibitor's sequence following their highest efficiency in 1 M H_2SO_4 is as follows:

MTB (94.0%) \approx SO (93.0%) \approx SS (92.5%).

At a concentration of 1×10^{-4} M the line changes to:

OS (92.5%) \approx SS (91.0%) > MTB (60.0%)

The line is OS > SS > MTB at lower concentration values.

The results of the gravimetric investigation show that all three compounds have inhibitive properties in 1 M HCl and 1 M H_2SO_4 . The latter results are slightly better than those in HCl. The difference is better outlined in presence of MTB.

OS provides the best protective properties in 1 M HCl in the whole concentration range studied. It is also the best inhibitor among those investigated in 1 M H_2SO_4 at the concentration values used. In fact MTB is slightly better but at concentrations higher than OS maximal concentration studied. The latter is in fact insoluble at these MTB concentrations.

The protective properties of OS and SS are quite similar in both media investigated with a slight dominance of OS.

3.1.2. Potentiodynamic voltammetry tests

The potentiodynamic voltammetry investigations are carried out in 1 M HCl at various concentrations of the inhibitors. The polarization curves recorded provide the determination of the electrochemical parameters as the corrosion current density, j_{corr} , the corrosion potential, E_{corr} , the cathodic and anodic Tafel slopes, b_c and b_a , correspondingly, the polarization resistance, R_p . The variation of the electrochemical parameters provides to follow the effect of the inhibitors on the kinetics of the corrosion process. The values obtained are listed in Table 2. Typical polarization curves are shown in Fig.3.

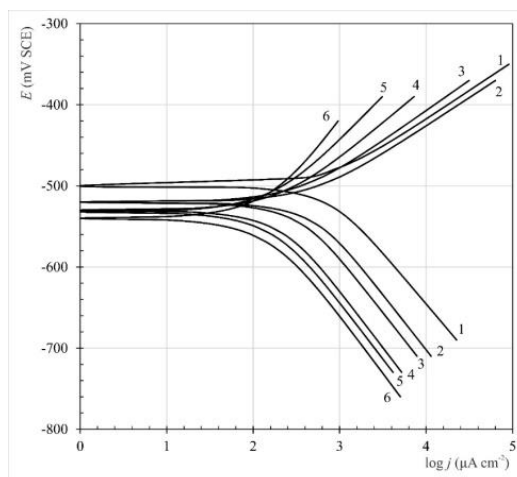


Fig. 3. Potentiodynamic polarization curves in presence of SS: 1 – 1 M HCl; 2 – 1×10^{-6} M; 3 – 1×10^{-5} M; 4 – 1×10^{-4} M; 5 – 5×10^{-4} M; 6 – 1×10^{-3} M.

Table 2. Electrochemical parameters obtained from the polarization curves of bromides studied

Methylbenzo[d]thiazol-3-ium bromide, MTB

c_i (M)	E_{corr} (mV)	$-b_c$ (mV/dec)	b_a (mV/dec)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	χ^2	R_p ($\text{k}\Omega \text{ cm}^2$) \square	$j_{corr}^{R_p}$ ($\mu\text{A}/\text{cm}^2$)
1MHCl	-498 ± 2	126 ± 4	71 ± 5	700 ± 50	5.0 ± 1.5	0.0340 ± 0.0050	690 ± 48
1×10^{-5}	-500 ± 3	128 ± 5	76 ± 7	728 ± 44	8 ± 3	0.0338 ± 0.0080	729 ± 61
1×10^{-4}	-498 ± 2	132 ± 5	81 ± 6	687 ± 45	9 ± 3	0.0349 ± 0.0071	651 ± 39
1×10^{-3}	-495 ± 1	136 ± 6	92 ± 4	441 ± 18	11 ± 2	0.0528 ± 0.0078	438 ± 21
5×10^{-3}	-491 ± 3	137 ± 4	98 ± 5	300 ± 14	12 ± 3	0.0835 ± 0.0063	292 ± 10
1×10^{-2}	-488 ± 1	135 ± 5	98 ± 3	228 ± 6	12 ± 4	0.1020 ± 0.0058	227 ± 7
2×10^{-2}	-488 ± 1	138 ± 4	100 ± 2	216 ± 4	10 ± 2	0.1156 ± 0.0049	217 ± 5

3,4-Dihydro-2H-benzo[4,5]thiazolo[2,3-b][1,3]thiazin-5-ium bromide, SS

c_i (M)	E_{corr} (mV)	$-b_c$ (mV/de c)	b_a (mV/de c)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	χ^2	R_p ($\text{k}\Omega \text{ cm}^2$)	$j_{corr}^{R_p}$ ($\mu\text{A}/\text{cm}^2$)
1×10^{-6}	-520 ± 2	136 ± 3	70 ± 4	458 ± 47	35 ± 2	0.0516 ± 0.0084	464 ± 71
1×10^{-5}	-520 ± 3	136 ± 4	75 ± 4	315 ± 16	24 ± 4	0.0815 ± 0.0034	300 ± 19
1×10^{-4}	-530 ± 2	140 ± 4	89 ± 2	195 ± 12	6 ± 2	0.1047 ± 0.0055	207 ± 8
5×10^{-4}	-532 ± 2	140 ± 5	110 ± 7	160 ± 4	18 ± 1	0.1443 ± 0.0038	164 ± 2
1×10^{-3}	-540 ± 2	143 ± 4	145 ± 11	146 ± 6	5.7 ± 2	0.1639 ± 0.0050	148 ± 12

3,4-Dihydro-2H-benzo[4,5]oxazolo[2,3-b][1,3]thiazin-5-ium bromide, OS

c_i (M)	E_{corr} (mV)	$-b_c$ (mV/de c)	b_a (mV/de c)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	χ^2	R_p ($\text{k}\Omega \text{ cm}^2$)	$j_{corr}^{R_p}$ ($\mu\text{A}/\text{cm}^2$)
1×10^{-7}	-510 ± 5	136 ± 3	69 ± 4	530 ± 51	9 ± 2	0.0484 ± 0.0014	551 ± 41
1×10^{-6}	-510 ± 4	131 ± 4	75 ± 4	337 ± 60	22 ± 4	0.0789 ± 0.0112	348 ± 29
1×10^{-5}	-513 ± 4	131 ± 5	96 ± 2	253 ± 32	65 ± 12	0.0819 ± 0.0075	266 ± 8
1×10^{-4}	-517 ± 2	139 ± 5	119 ± 7	179 ± 4	3 ± 1	0.1360 ± 0.0138	180 ± 2
5×10^{-4}	-526 ± 2	153 ± 4	165 ± 18	141 ± 5	4 ± 2	0.1719 ± 0.0130	142 ± 12

With concentration increase E_{corr} shifts in a positive direction in presence of MTB, while the presence of SS and OS brings about a shift in the opposite direction. The values of the Tafel slopes, b_c and b_a , increase with the increase of all compounds concentration. The highest values are obtained at the highest concentration of OS. The results pointed above lead to the conclusion that all compounds are in fact general mixed type inhibitors. MTB shows slightly better expressed anodic behavior, while that of SS and OS tends to the cathodic one.

The corrosion current density, which is a measure of the corrosion rate decreases with increase of the inhibitor's concentration, c_i . This is valid for all compounds studied. The inhibiting efficiency, IE (%), is evaluated on the ground of the values of j_{corr} with the application of Eq. (2). The dependence of IE (%) on c_i is presented in Fig. 4. It is evident that the inhibiting effect increases with the concentration increase in case of all compounds studied. This result is in correspondence with the gravimetric findings. It is worth noting that the values of IE (%) found potentiodynamically are generally lower than those obtained gravimetrically. This is most probably due to the different exposure time in the solution – it is 24 h in the course of the gravimetric tests, while the polarization curves are potentiodynamically recorded immediately after the electrode immersion. Irrespective of this difference the sequence of the inhibitors in respect to their efficiency stays unchanged.

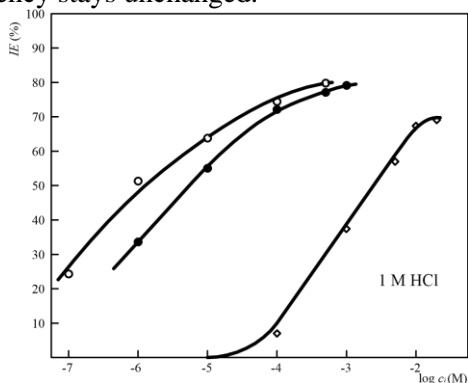


Fig. 4. Dependence of the inhibiting efficiency, IE (%), on the inhibitors concentration, c_i (M) obtained on the ground of the potentiodynamic voltammetric data obtained: OS (\circ), SS (\bullet) and MTB (\diamond).

Thus the inhibitors line obtained on the ground of the highest effect recorded at the highest available concentration is as follows: OS (79.8%) \approx SS (79.19%) $>$ MTB (69.1%).

At a concentration of 1×10^{-4} M the line becomes: OS (74.4%) \approx SS (72.1%) $>$ MTB (10.0%). At lower concentration the difference between the behavior of OS and that of SS becomes more distinct. It has to be underlined that the lines just presented coincide with those obtained gravimetrically in 1 M HCl.

The values of the polarization resistance, R_p , increase with the increase of the compounds' concentration. This is an additional verification of the protective properties improvement. The values of j_{corr} determined on the ground of the R_p - method almost coincide with those evaluated by the Tafel plot-method. This is so because identical polarization curves are used.

The results obtained with potentiodynamic voltammetry application show that OS has the best protective properties in the whole concentration range studied. It is closely followed by SS. It can be concluded that the molecular structure affects also the inhibitive properties displayed.

3.2. Adsorption parameters

The organic substances molecules or ions adsorption on the metal surface is the fundamental cause for decrease of the corrosion rate in an acid medium. The experimental results obtained provide to choose an appropriate adsorption isotherm, whose application leads in turn to the elucidation of some of the peculiarities of the adsorption process taking place.

In this study the degree of fractional surface coverage, θ , is calculated using the kinetic data obtained. The relation $\theta = IE$ (%) / 100 [11, 13, 54] is used. The value of IE (%) is obtained on the ground of the gravimetric measurements as it is assumed that the adsorption/desorption equilibrium is reached within the 24 h of specimens immersion in the solution. The adsorption isotherms of Langmuir, Frumkin and Temkin are usually applied [55] in the field. It is found that Frumkin's isotherm provides the best description of the adsorption data. It is usually presented in the form:

$$Bc = \frac{\theta}{1-\theta} \exp(-2a\theta), \quad (3)$$

where θ is the fractional surface coverage, a is the interaction parameter, c is the concentration, while B is an adsorption parameter, which has the meaning of the adsorption/desorption equilibrium constant. B is related to the standard free energy of adsorption, ΔG_{ads}^0 , in correspondence with the equation:

$$B = \frac{1}{55,5} \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad (4)$$

The adsorption parameters are evaluated using the non-linear procedure based on the least squares method described in ref. [54]. The experimental points and the curves of the adsorption isotherms

calculated are shown in Figs. 1 and 2. It is seen that the curves correspond well to the experimental points. This is also evident from the values of the standard deviation. They, as well as all other adsorption parameters obtained for both acidic solutions used, are summarized in Table

Table 3. Adsorption parameters determiner for quaternary ammonium bromides as inhibitors of mild steel corrosion.

Compounds	MTB	SS	OS
1 M HCl			
log <i>B</i>	4.04	6.76	7.48
<i>a</i>	1.54	1.65	2.17
ΔG_{ads}^0 , kJmol ⁻¹	-32.4	-47.7	-51.7
Standard Deviation	3.2x10 ⁻²	5.1x10 ⁻³	5.5x10 ⁻³
$-\log c_{\theta=0.5}$	4.71	7.47	8.42
1M H₂SO₄			
log <i>B</i>	4.04	7.86	7.90
<i>a</i>	- 0.35	2.97	2.02
ΔG_{ads}^0 , kJmol ⁻¹	-32.5	-53.88	-54.11
Standard Deviation	2.5x10 ⁻³	8.4x10 ⁻²	3.7x10 ⁻³
$-\log c_{\theta=0.5}$	3.89	9.15	8.78

The interaction constant *a* has positive values for all compounds investigated in 1 M HCl. This indicates the presence of forces of attraction between the species adsorbed, which in fact facilitate the further adsorption proceeding in the monolayer.

The results referring to H₂SO₄ medium are similar. MTB is the only exclusion as constant *a* has a negative value (*a* = - 0.35) in this case. This is most probably due to *a* compensation effect - the attraction observed between the molecules adsorbed on the metal surface is partially compensated by the latter energetic inhomogeneity. This provides the formal validation of the Langmuir isotherm although the assumptions required in the course of its derivation are not present.

The values of ΔG_{ads}^0 are negative for all substances in both media investigated. This is a thermodynamic verification of the fact that the adsorption is spontaneously proceeding.

The juxtaposition of the inhibitors in view of the absolute value of ΔG_{ads}^0 obtained in their presence results in the following lines: OS > SS > MTB in 1 M HCl, while OS ≈ SS > MTB in 1 M H₂SO₄ medium. The same lines are obtained if the values of log*B* are taken into account. It is worth adding that this type of arrangement corresponds to the one

obtained on the ground of the inhibitor efficiency observed at a concentration value of 1x10⁻⁴ M.

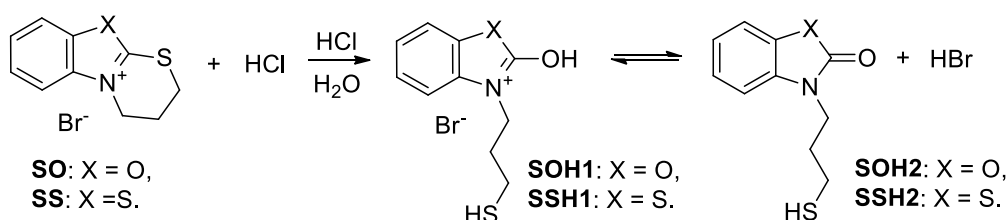
3.3. On the inhibiting activity/molecular structure relation

The different inhibiting properties shown by the three compounds obtained in the course of study with the application of different methods are due to the difference in their molecular structure.

The quaternary ammonium bromides dissociate in acidic solutions giving ammonium cations and a bromine anion, Br⁻. We assume that the cation structure determines the difference of the inhibitive properties. The effect of Br⁻ presence in the solution cannot be excluded because of this anion disposition to specific adsorption on the metal surface [4, 5]. This can result to a change of the surface charge or a synergistic effect, i.e. Br⁻ contribute to the inhibiting effect observed. On the other hand, Br⁻ can favor the adsorption by decreasing the cations repulsion in the adsorption layer (the positive values of the interaction adsorption parameter indicate actual attraction in the adsorption layer).

We assume that the juxtaposition of MTB on one hand and SS and OS on the other can outline the effect of the adsorbed species surface area (in fact of the cationic part in this case), while the

comparison between SS and OS can illustrate the dependence on the electron structure as both compounds have an almost identical surface area (the difference is determined by the dimensions of the S and O atom present). The experimental results show that MTB is a weaker inhibitor when compared to SS and OS at an identical concentration. This is most probably due to the smaller surface of its cationic part. The protective properties of OS are better than those of SS but the difference observed decreases with concentration increase. In view of the molecular structure only (Table 1) the inhibiting properties should be identical or a slightly better performance can be expected in case of SS as the S atom is a better electron couple donor when compared with the O atom.



Scheme 1

Furthermore the presence of the basic form of SS and OS in the solution cannot be excluded (the dihydrothiazonium ring is not ruptured in this case). The dynamic equilibria of the three forms of the compounds, i.e. SO, SOH1 and SOH2 on one hand, and SS, SSH1 and SSH2 on the other, determine the difference in the inhibitive properties displayed. Most probably they also affect the solubility observed.

At this stage of our investigations we assume a probability of Br^- specific adsorption on the metal surface in both acidic solutions. This brings about a negative charge to the surface and explains the relatively close inhibiting efficiency in both acids. This effect can also favor the physical adsorption of the molecules cationic part.

CONCLUSIONS

The three compounds investigated show protective properties in case of mild steel corrosion in 1 M HCl and 1 M H_2SO_4 . Their inhibiting effect increases with their concentration increase. OS acts as the best inhibitor in the concentration range from 1×10^{-6} M. It is closely followed by SS.

The adsorption of two of the bromides on the metal surface is described by the adsorption isotherm of Frumkin or that of Langmuir (MTB in 1 M H_2SO_4). Positive values of the constant of interaction are found in most of the cases, which

Why is this unexpected effect of the electronic structure? The cationic part of SS refers to a benzothiazole heterocycle containing fused dihydrothiazinium heterocycles at positions 2 and 3, while the cationic part of SO consists of a benzoxazole heterocycle with fused dihydrothiazinium heterocycle at the same positions, i.e. the substituents and their positions are identical. The dihydrothiazinium ring ruptures under the effect of the acidic aqueous medium and a propanethiole substituent appears at position 3 in the basic heterocycle of OS and SS. Thus two tautomeric forms appear which stay in a dynamic equilibrium. The first one refers to oxazole (SOH1) and oxazolone (SOH2), while the second one - to thiazole (SSH1) and thiazolone (SSH2).

indicates that the species adsorbed attract the adsorbing one facilitating the adsorption itself.

The results obtained show that the molecular structure affects essentially the inhibitive properties when compared at identical concentrations. It is not possible to conclude explicitly which parameters of the molecular structure are of predominating importance. In the case studied OS and SS change their structure and in fact three different species take part in the adsorption proceeding. We assume that physical adsorption of the molecules cationic parts takes place at the negatively charged metal surface.

REFERENCES

1. L. L. Shrier (ed.), Corrosion, Metallurgia, Moscow, 1981.
2. N. P. Zhuk, Course of Corrosion and Metal Protection (Russ.), Metallurgia, Moscow, 1976.
3. P. R. Roberge, Handbook of Corrosion Engineering, McCrow-Hill, N.Y., 2000.
4. S. M. Reshetnikov, Acid Corrosion Inhibitors of the Metals (Russ.), Khimia, Leningrad, 1986.
5. I.L. Rozenfeld, Corrosion inhibitors (Russ.), Khimiya, Moscow, 1977.
6. L.I. Antropov, E. M. Makushin, V. F. Panasenko, Metal Corrosion Inhibitors (Russ.), Technika, Kiev, 1981.
7. Z.A. Foroulis, in: Proceedings of 6th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, N. S. Sez. V, Suppl. N8, 1985.

8. F. Zucchi, G. Trabaneli, in: Proceedings of 7th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, N. S. Sez. V, Suppl. N9, 1990.
9. R.C. Ayers, N. Hackerman, J. Electrochem. Soc., **110**, 507 (1963).
10. T. Szauder, A. Brandt, Electrochim. Acta, **26**, (1981) 1209-1217.
11. J. de Damborenea, J. M. Bastidas and A. J. Vázquez, Electrochim. Acta, **42**, 455 (1997).
12. D.A. Lopez, S.N. Simison, S.R. de Sanchez, Electrochim. Acta, **48**, 845 (2003).
13. G. Moretti, G. Quartarone, A. Trassan, A. Zingales, Electrochim. Acta, **41**, 1971 (1996).
14. E. Garcia-Ochoa, J. Genesca, Surf. Coat. Technol., **184**, 322 (2004).
15. S.L. Li, Y.G. Wang, S.H. Chen, R. Yu, S.B. Lei, H.Y. Ma, De X. Lin, Corros. Sci., **41** 1769 (1999).
16. K. Babić-Samardžija, N. Hackerman, J. Solid State Electrochem., **9**, 483 (2005).
17. H. L. Wang, R.-B. Liu, J. Xin, Corros. Sci., **46**, 2455 (2004).
18. M. Özcan, I. Dehri. M. Erbil, Appl. Surf. Sci., **236**, 155 (2004).
19. H. Keleş, M. Keleş, I. Dehri, O. Serindağ, Colloids Surf. A: Physicochem. Eng. Aspects, **320**, 138 (2008).
20. M.S. Morad, Corros. Sci., **50**, 436 (2008).
21. E. Chaieb, A. Bouyanzer, B. Hammouti, M. Benkaddour, Appl. Surf. Sci., **246**, 199 (2005).
22. A. Dutta, S. K. Saha, P. Banerjee, D. Sukul, Corros. Sci., **98**, 541, (2015).
23. H. Zarrok, A. Zarrouk, R. Salghi, B. Elmahi, B. Hammouti, S.S. Al-Deyab, M. Ebn Touhami, M. Bouachrine, H. Oudda, H. Boukhris, Int. J. Electrochem. Sc., **8**, 11474 (2013).
24. Ostapenko, G.I., Gloukhov, P.A., Bunev, A.S., Corros. Sci., **82**, 265 (2014).
25. A. S. Fouda, A. H. Soliman, Prot. Met. and Phys. Chem. of Surfaces, **51**, 847 (2015).
26. I. B. Obot, A. Madhankumar, S.A. Umoren, Z. M. Gasem, J. Adhes. Sci. Technol., **29**, 2130, (2015).
27. H. M. Abd El-Lateef, Corros. Sci., **92**, 104, (2015).
28. D. Zhang, Y. Tang, S. Qi, H. Cang, G., Corros. Sci., **102**, 517, (2016).
29. E. Gutiérrez, J. A. Rodríguez, J. Cruz-Borbolla, J. G. Alvarado-Rodríguez, P. Thangarasu, Corros. Sci., **108**, 23 (2016).
30. A. Stoyanova, E. Slavcheva, Mater. Corros., **62**, 872 (2011).
31. A. Popova, M. Christov, S. Raicheva, E. Sokolova, Corros. Sci., **46**, 1333 (2004).
32. A. Popova, M. Christov, T. Deligeorgiev, Corrosion, **59**, 756, (2003).
33. A. Popova, M. Christov, A. Zwetanova, Corros. Sci., **49**, 2131, (2007).
34. A. Popova, M. Christov, A. Vasilev, A. Zwetanova, Corros. Sci. **53**, 679, (2011).
35. G. Schmitt, in: Proceedings of 6th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, N. S. Sez. V, Suppl. N. 8, 1985.
36. G. Schmitt, K. Bedburg, in: Proceedings of 9th International Congr. Metallic Corrosion, Toronto, 1984, p. 112.
37. K.F. Khaled, Appl. Surface Sci., **236**, 307 (2004).
38. L. Tang, X. Li, G. Mu, G. Liu, L. Li, H. Liu, Y. Si, J. Mater. Sci., **41**, 3063 (2006).
39. M.M. Saleh, A.A. Atia, J. Appl Electrochem., **36**, 899, (2006).
40. M.M. Saleh, Mat. Chem. Phys., **98**, 83, (2006).
41. L.G. Qiu, Y. Wu, Y.M. Wang, X. Jiang, Corros. Sci., **50**, 576, (2008).
42. X. Li, L. Tang, H. Liu, G. Mu, G. Liu, Mater. Lett., **2**, 2321, (2008).
43. A.A. Hermas, M.S. Morad, M.H. Wahdan, J. Appl. Electrochem., **34**, 95, (2004).
44. H. Ashassi-Sorkhabi, M. Es'haghi, Mat. Chem. Phys., **114**, 267, (2009).
45. R. Fuchs-Godec, Electrochim. Acta, **54**, 2171, (2009).
46. M. A. Hegazy, A. A. Nazeer, K. Shalabi, J. Mol. Liq., **209**, 419, (2015).
47. M. A. Hegazy, M. Abdallah, M. K. Awad, M. Rezk, Corros. Sci., **81**, 54 (2014).
48. M. A. Hegazy, A. M. Badawi, S. S. Abd El Rehim, W. M. Kamel, Corros. Sci., **69**, 110, (2013).
49. P. Mourya, P. Singh, A. K. Tewari, R. B. Rastogi, M. M. Singh, Corros. Sci., **95**, 71 (2015).
50. A. Popova, M. Christov, A. Vasilev, Corros. Sci., **49**, 3276, (2007).
51. T. Deligeorgiev, N. Gadjev, A. Vasilev, R. Drexhage, S. Yarmoluk, Dyes and Pigments, **70**, 185 (2006).
52. A. Popova, S. Veleva, S. Raicheva, React. Kinet. Catal. Lett., **85**, 99, (2005).
53. M. Stern, A.L. Geary, J. Electrochem. Soc., **104**, 56 (1957).
54. M. Christov, A. Popova, Corros. Sci., **46**, 1613, (2004).
55. B. Damaskin, O. A. Petrii, V. V. Batrakov, Organic Compounds Adsorption on Electrodes (Russ.), Metalurgia, Moscow, 1976.