Aminotris(methylenephosphonic acid) and sodium gluconate as inhibitors of carbon steel corrosion in 3.5% NaCl solution

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Abstract

Corrosion inhibition of carbon steel (RSt 37-2) protected by mixtures of aminotris (methylenephosphonic acid) (ATMP) and sodium gluconate (SG) in 3.5% NaCl solution has been studied. The effect of combined action of ATMP and SG has been evaluated using Tafel polarization and microscopy techniques. SG and ATMP were added in low concentrations. Concentration range of SG was from 1 mM to 10 mM, and ATMP was added in concentrations from 1 to 6 mM ($\text{mmol}\cdot\text{L}^{-1}$). As control experiment, corrosion inhibition efficiencies of SG and ATMP on carbon steel corrosion in 3.5% NaCl were separately evaluated in one inhibitor system. Afterwards, inhibitors were employed in mixtures (two inhibitors system). In both experiments the majority of employed inhibitor concentrations significantly decreased corrosion current. When employed alone both inhibitors were more susceptible to pitting corrosion or excessive oxidation product formation. When employed in mixtures some inhibitor combinations, primarily those that were composed of moderate concentrations of both inhibitors, exhibited excellent general and pitting corrosion inhibition. When using SG as only inhibitor anodic inhibition mechanism was observed, whereas ATMP alone acted as cathodic inhibitor. Using both inhibitors predominant mechanism of cathodic inhibition was observed. The results clearly showed that carefully selected mixtures of ATMP and SG could successfully inhibit corrosion of carbon steel in 3.5% NaCl solution.

Keywords: *carbon steel, corrosion inhibitors, sodium gluconate, aminotris(methylenephosphonic acid), NaCl solution.*

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1. Introduction

Seawater and different brines are increasingly used in industrial practice (cooling water systems, desalination plants, injection water, firefighting, ballast, pressure testing of pipelines) due to the both economic and ecological grounds. Since seawater is complex mixture containing many different salts, dissolved gases, trace elements, suspended solids, decomposed organic matter, and living organisms which composition varies on everyday basis it is not easily simulated in the laboratory for corrosion testing purposes. A 3.5% NaCl solution is used frequently for this purpose and is known to be more aggressive toward carbon steel than natural seawaters [1, 2].

Carbon and low-alloy steels are low-initial cost alloys and are the most widely used materials for the marine environment, for both structural components and pressure-retaining applications. If appropriate protective measures are not used they have high maintenance and replacement costs [1]. In saline conditions carbon steels are highly susceptible to corrosion attack (general, localized and galvanic corrosion). Their protection is accomplished using protective coatings, corrosion inhibitors, galvanic protection or their combination [1, 3].

Highly toxic substances such as chromates, dichromates and nitrites that were widely and effectively used for corrosion protection are, due to increasingly more stringent environmental regulations, replaced by more environment friendly components [4]. Environmentally acceptable inhibitors are those inhibitors which, in applied concentrations, do not disturb ecological balance or take negative impact on human health. They can be divided in three groups: inorganic substances such as rare-earth metal (REM) salts, borates, silicates, molybdates; organic compounds such as thioglycolates, phosphonates, sulfonates, carboxylic acids and their salts (amino acids, fatty acids, gluconates), vitamins, pigments, antibiotic or antifungal drugs (*e.g.* imidazole compounds), alkaloids (nicotine, caffeine); and true "green" inhibitors such as various herbal extracts (water, alcohol or acid extracts) [3]. Extracts of natural plants are not expensive, environmentally acceptable and easily biodegradable. However, this biodegradability limits the storage and long-term usage of plant extracts [5]. Since they are complex mixtures of variety of compounds with uncertain exact composition it is not easy to predict their inhibitory action. Therefore, they are still rarely commercially applied in spite their ever growing popularity in numerous scientific researches.

Gluconates are environmentally suitable non-toxic compounds having also useful applications in medicine. The efficiency and the mechanism of the corrosion inhibition by gluconates, either as single compound or in a mixture, have been described in a number of recent studies [2, 3, 6–8]. Gluconates are part of the successful commercial corrosion inhibitors and are recommended in mixture with water soluble polymeric dispersant, organophosphonate and silicate [9].

Phosphonates have been widely used as water treatment agents because of their high hydrolytic stability, ability to form a complex with metal ions, scale and corrosion inhibition activity in neutral aqueous media. They are eco-friendly and relatively less expensive compounds [10, 11]. In addition, even low concentrations are required for the protection of large water supply systems [12]. ATMP is an environmentally suitable organic phosphonate compound, which is mainly used in open water circulation cooling system, petroleum pipelines and boilers as scale and corrosion inhibitor [13]. It can be applied with other inhibitors, most notably Zn^{2+}, in well or saline waters, and in those mixtures can have a prominent synergistic effect on mild steel corrosion [10, 14]. It is often recognized as a mixed type corrosion inhibitor [10].

2. Experimental

The electrochemical experiments were performed using carbon steel EN S235 JRG of following composition: C 0.17%, P 0.05%, S 0.058%, N 0.007%, Si 0.19%, Mn 0.42%. Working electrode area was 1 cm^2. Before measurements the specimen was polished with emery paper (400, 600, 800 and 1200 grade) degreased with ethanol and rinsed with demineralised water. Afterwards the working electrode was immersed in electrochemical cell containing 600 ml of investigated medium. All experiments were performed at ambient temperature (22 ± 2°C). The electrochemical cell was equipped with graphite auxiliary electrode and a reference saturated calomel electrode which was connected to the working electrode over Luggin capillary. Electrochemical measurements were performed on Potentiostat/Galvanostat EG&G PAR, Model 273 A using software SoftCorr III. The open circuit potential (OCP) was measured as a function of time in order to understand the corrosion behaviour of the sample in the electrolyte. A soon as the sample was immersed into the electrolyte, the initial potential of the sample was noted and monitored as a function of time until the sample attained a constant potential E_{corr} (typically 30–60 min). The method of quasi potentiostatic polarization or the Tafel extrapolation method was carried out recording polarization curves in the range ±250 mV from the corrosion potential (E_{corr}) with a polarization rate $0.166\ \mathrm{mV \cdot s^{-1}}$. From Tafel polarization curves following corrosion parameters were calculated: the corrosion current density (j_{corr}) and the inhibition coefficient (Z) was calculated using Equation 1. All results are given with the expanded measurement uncertainty $U = 15.0\ \mu\mathrm{A/cm^2}$ with the coverage factor $k = 2$ and the coverage probability $p = 95\%$.

$$Z = \frac{j_{\mathrm{ni}} - j_{\mathrm{inh}}}{j_{\mathrm{ni}}} \tag{1}$$

Z – inhibition coefficient
j_{ni} – corrosion current density in an uninhibited experiment ($\mu\mathrm{A \cdot cm^{-2}}$)
j_{inh} – corrosion current density in an inhibited experiment ($\mu\mathrm{A \cdot cm^{-2}}$)

Experiments were performed in 3.5% NaCl solution. For electrolyte (media) preparation aminotris (methylenephosphonic acid) (*p.a.* Merck) and sodium gluconate (*p.a.* Alfa Aesar) were used. Prior to electrochemical measurements, pH of inhibitor solutions was adjusted to 7.00 ± 0.02 with 0.1 M ($\mathrm{mol \cdot L^{-1}}$) NaOH. After electrochemical measurements, the surface of the steel specimen was observed and photographed using stereomicroscope LeicaMZ6. For weighting of ATMP and SG a Kern ABS 220-4 balance (±0.0002 g) was used.

3. Results and Discussion

3.1. The effect of SG and ATMP addition on corrosion inhibition in 3.5% NaCl – one inhibitor

In order to separately evaluate corrosion inhibition efficiency of SG and ATMP addition on carbon steel corrosion in 3.5% NaCl different concentrations of inhibitors were employed in one inhibitor system. An experiment without inhibitor addition was also performed. Tafel polarization curves are presented in Figures 1 and 2 and corrosion parameters on Table 1. SG and ATMP were added in small amounts. Concentration range of SG was from 1 mM to 10 mM, and ATMP was added in concentrations from 1 to 6 mM (mmol·L^{-1}). All employed SG concentrations had tendency to shift E_{corr} value in the positive direction when compared to uninhibited curve (Figure 1). All employed SG concentrations considerably decreased corrosion current notably to similar extent (with exception of 1 mM, Table 1). These results are in concordance with previous findings [3, 6].

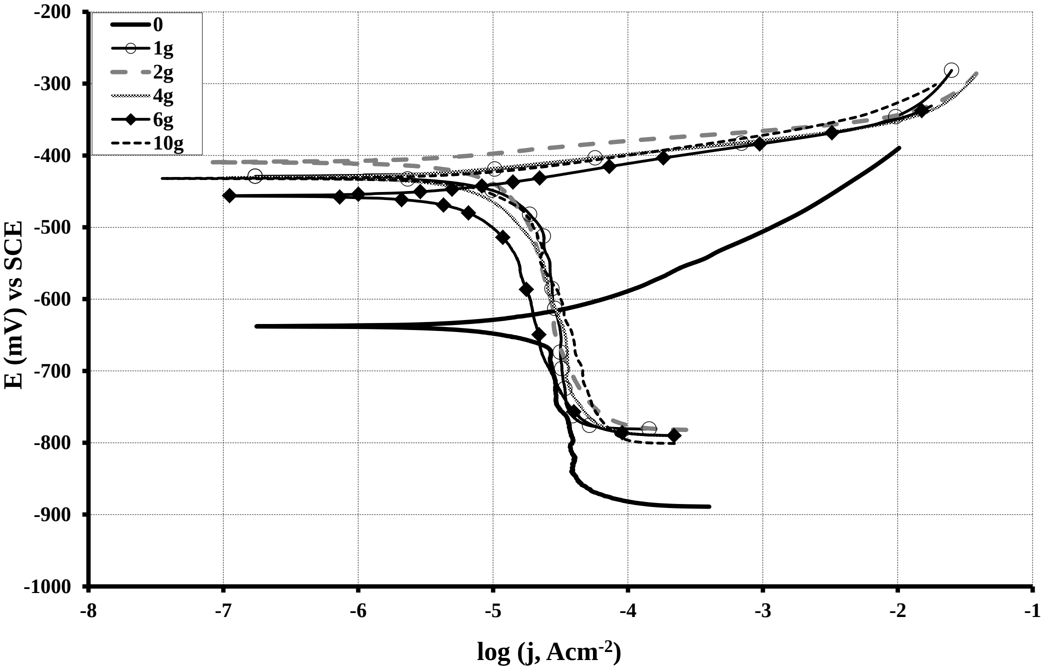


Figure 1. Tafel polarization curves of carbon steel in 3.5% NaCl – SG addition (number in legend represents mM of SG (g)).

Opposite to SG experiments, ATMP had tendency to shift E_{corr} value in the negative direction when compared to uninhibited curve (Figure 2, Table 1). The results coincide with previously published articles [15, 16]. Similar to SG, all employed ATMP concentrations considerably decreased corrosion current to similar extent (72–81%, Table 1).

Despite fairly good corrosion current decrease, after electrochemical measurements the surfaces of the carbon steel specimens were either showing oxidation product formation (*i.e.* Figure 3, 2 SG, 6 ATMP) or pitting formation (Figure 3, 6 SG, 1 and 2 ATMP).

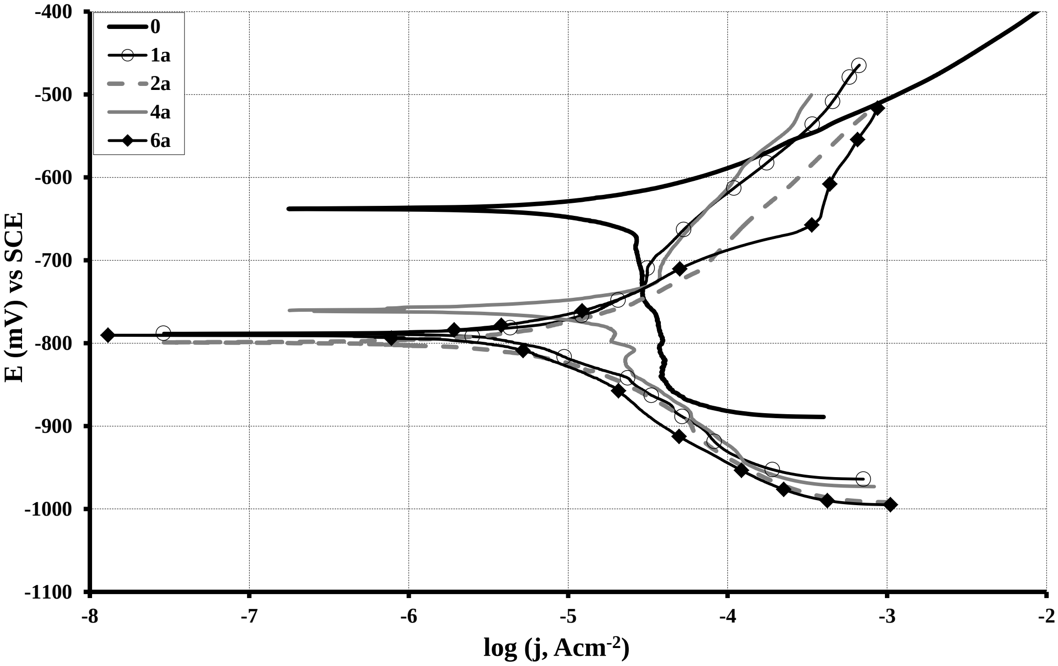
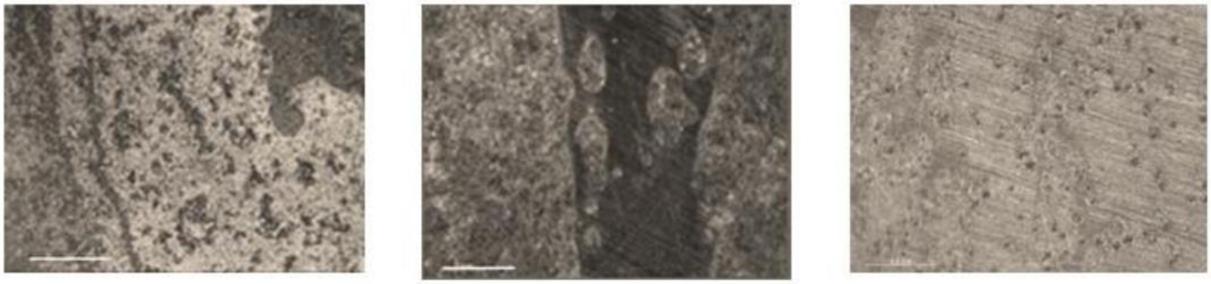


Figure 2. Tafel polarization curves of carbon steel in 3.5% NaCl – ATMP addition (number in legend represents mM of ATMP (a)).

Therefore, giving the fact that surfaces of the carbon steel specimens after electrochemical research are still not well protected in 3.5% NaCl medium, exhibiting general or pitting corrosion occurrence, further experiments were performed by mixing SG and ATMP. It can be concluded that SG acts as anodic inhibitor and ATMP as cathodic inhibitor on employed carbon steel in 3.5% NaCl medium.

Table 1. Corrosion parameters of carbon steel in 3.5% NaCl solution – one inhibitor.

Inhibitor concentration, mM		**E_{corr}, mV**	**j_{corr}, µA·cm^{-2}**	***Z***
–		–631	42.41	0
SG	1	–429	17.02	0.6
SG	2	–409	10.53	0.75
SG	4	–431	10.36	0.76
SG	6	–456	8.54	0.8
SG	10	–432	11.79	0.72
ATMP	1	–788	10.68	0.75
ATMP	2	–799	9.32	0.78
ATMP	4	–761	11.96	0.72
ATMP	6	–790	7.94	0.81



Without inhibitor 2 SG 6 SG

1 ATMP 2 ATMP 6 ATMP

Figure 3. Surface of the carbon steel specimens after electrochemical measurements in 3.5% NaCl solution – one inhibitor (white line at left lower corner represents 0.5 mm).

3.2. The effect of SG and ATMP addition on corrosion inhibition in 3.5% NaCl – two inhibitors mixtures

In order to determine possible synergistic or even antagonistic effect on corrosion inhibition, ATMP was supplemented with SG in two-inhibitor media (Table 2). Tafel polarization curves are presented in Figures 4–7. Surfaces of the carbon steel specimens after electrochemical measurements are shown in Figure 8. Almost all of the inhibitor combinations showed substantial corrosion rate reduction compared to uninhibited medium. Moreover, all inhibitor combinations had tendency to shift E_{corr} value in the negative direction when compared to uninhibited curve, thereby acting predominately as cathodic inhibitors.

Experiments with 1 mM of ATMP (Figure 4, Table 2), which was the lowest employed concentration of ATMP, showed fairly high corrosion inhibition. In this experimental set the best corrosion inhibition was achieved on medium that contained moderate SG concentration (4 mM). Inhibition efficiency of that inhibitor mixture reached 76% (Table 2).

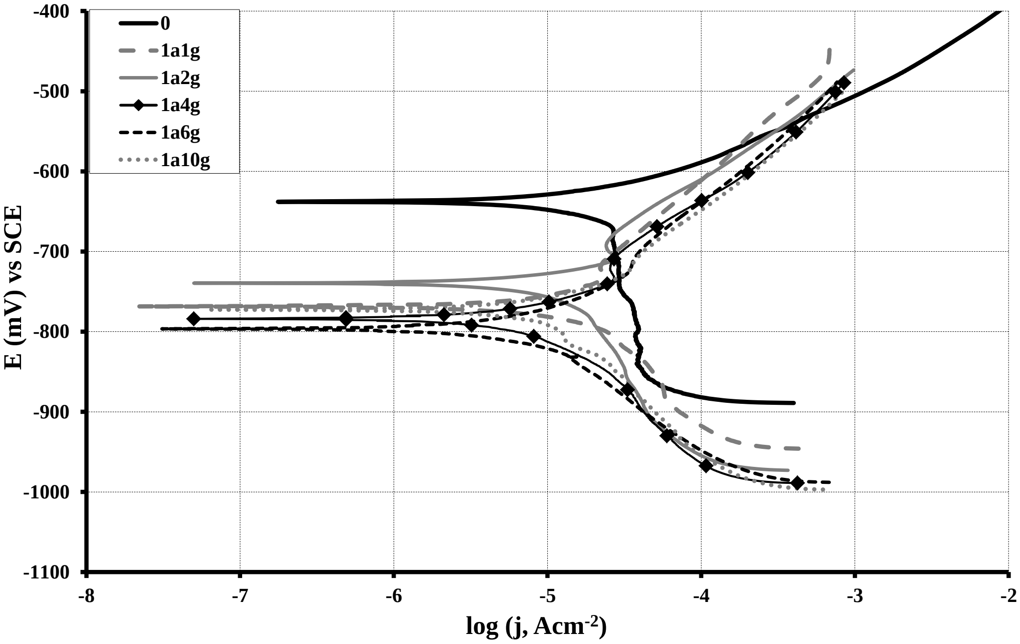


Figure 4. Tafel polarization curves of carbon steel in 3.5% NaCl – mixtures with 1 mM ATMP (numbers in legend represents mM; ATMP (a) and SG (g)).

At higher concentrations of ATMP (2 mM; Figure 5, Table 2) all combinations showed pronounced corrosion inhibition with values around 80%. Likewise, all combinations were very similar when Tafel curves were compared (Figure 4). The surfaces of the carbon steel specimens after electrochemical measurements (Figure 8) showed the development of pitting corrosion at lower and higher concentrations of SG. Therefore, combination with 2 mM of both ATMP and SG (84%, Table 2) was chosen as the best combination in this experimental set, given the fact that it displayed both excellent corrosion inhibition and, at the same time, carbon steel specimen surface that was without any signs of general or pitting corrosion after measurement. Although the synergy between inhibitors is not prominent, depending strongly on medium composition, it is nevertheless evident that certain mixtures of ATMP and SG can act in synergistic manner and protect carbon steel in aggressive medium such is 3.5% NaCl. For instance, when combination with 2 mM of both ATMP and SG is compared with one inhibitor experiments containing the same total inhibitor concentration, *i.e.* 4 mM of ATMP or SG it becomes clear that the mixture is superior to one inhibitor compositions (84% *vs.* 72 and 76% respectively, Tables 1 and 2). Moreover, lowering the necessary amounts of employed inhibitors due to the synergistic effect is favorable regarding the price of consequent inhibitor mixture and also more ecologically beneficial. Predominant mechanism of ATMP adsorption on carbon steel is physisorption as proposed in previous works [17]. It is well known that SG forms Fe^{2+}–gluconate that is adsorbed on anodic sites of the steel. In synergistic mixtures of both compounds it could be concluded that both ATMP and SG are forming thin protective layer that is adsorbed on steel surface.

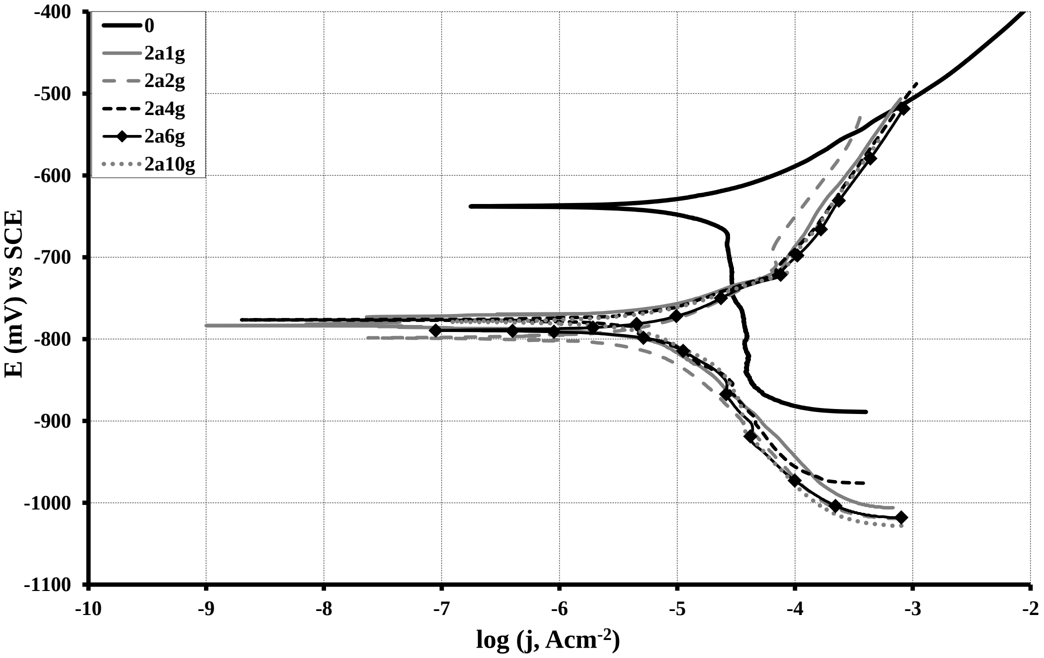


Figure 5. Tafel polarization curves of carbon steel in 3.5% NaCl – mixtures with 2 mM ATMP (numbers in legend represents mM; ATMP (a) and SG (g)).

At higher concentrations of ATMP (4 mM; Figure 6, Table 2) similar to previous experimental set, best inhibition was obtained using moderate concentrations. In this case it was combination with 4 mM of both ATMP and SG which reached 85% of inhibition efficiency and combination with 4 mM ATMP and 1 mM SG which reached efficiency of 84%. Higher concentrations of SG led to lower inhibition efficiency and development of pitting corrosion on the steel specimens (Table 2, Figure 8).

In last experimental set (6 mM of ATMP) corrosion inhibitor efficiency decreased significantly when compared to previous experimental sets (Figure 7, Table 2). Likewise, when compared to 6 mM of ATMP medium (without SG addition, Figure 2, Table 1) it is clear that the addition of SG decreased the efficiency of subsequent inhibitor. At that ATMP concentration (6 mM) addition of SG has antagonistic effect. When combinations containing the same total inhibitor concentration, *i.e.* 4 mM of both ATMP and SG and 6 mM ATMP and 2 mM SG, are compared it becomes obvious that the former is superior to latter (85% *vs.* 52%, Table 2). Similar antagonistic effects have been found for mild steel corrosion inhibition with phosphonate and silicate or polyacrylamide [18–20]. In antagonistic mixtures it could be concluded that interactions between ATMP and SG are aggravating the formation of their respective complexes with Fe^{2+} on the metal surface which is similar to previous findings on ATMP and polyacrylamide [20].

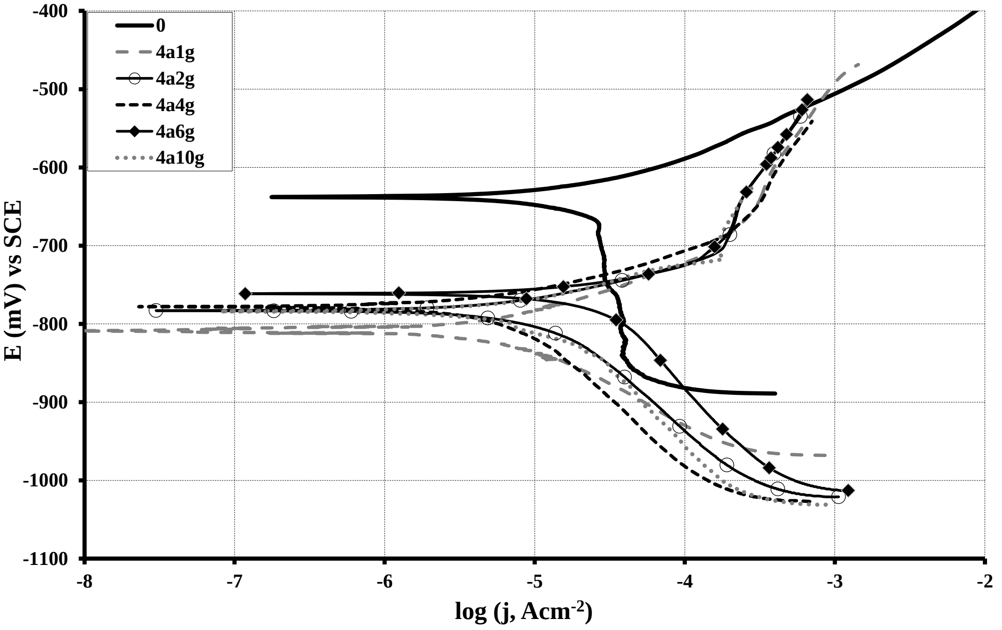


Figure 6. Tafel polarization curves of carbon steel in 3.5% NaCl – mixtures with 4 mM ATMP (numbers in legend represents mM; ATMP (a) and SG (g)).

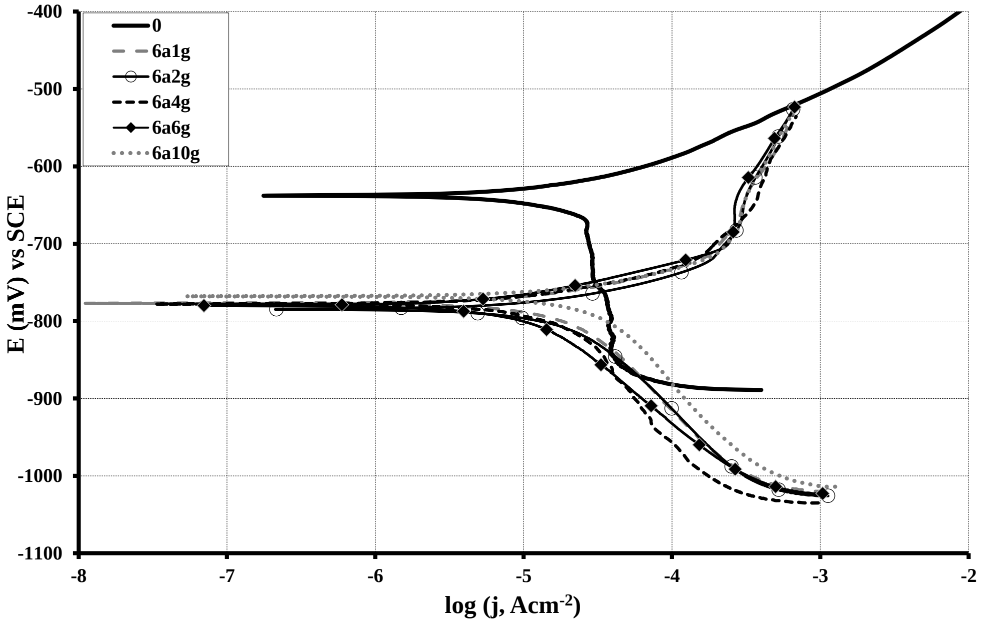


Figure 7. Tafel polarization curves of carbon steel in 3.5% NaCl – mixtures with 6 mM ATMP (numbers in legend represents mM; ATMP (a) and SG (g)).

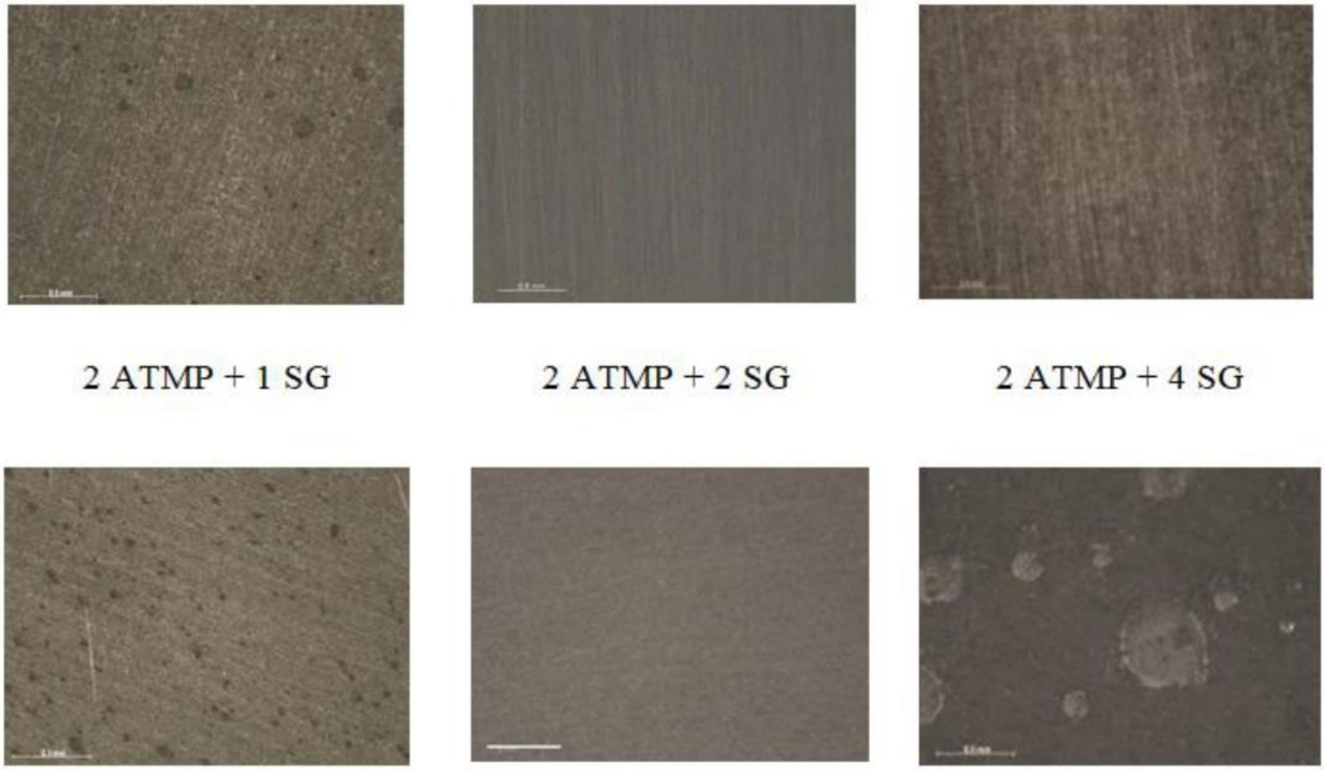


Figure 8. Surface of the carbon steel specimens after electrochemical measurements in 3.5% NaCl solution – two inhibitors mixtures (white line at left lower corner represents 0.5 mm).

Table 2. Corrosion parameters of carbon steel in 3.5% NaCl solution – two inhibitors mixtures.

Inhibitors concentrations, mM		E_{corr}, mV	j_{corr}, μAcm^{-2}	Z	Inhibitors concentrations, mM		E_{corr}, mV	j_{corr}, μAcm^{-2}	Z
ATMP	**SG**				**ATMP**	**SG**			
1	1	–768	16.37	0.61	4	1	–810	6.71	0.84
1	2	–739	16.78	0.60	4	2	–783	10.82	0.74
1	4	–784	10.02	0.76	4	4	–778	6.17	0.85
1	6	–797	12.05	0.72	4	6	–762	26.44	0.38
1	10	–772	13.83	0.67	4	10	–784	10.84	0.74
2	1	–780	7.09	0.83	6	1	–777	18.61	0.56
2	2	–799	6.76	0.84	6	2	–785	20.23	0.52
2	4	–779	7.86	0.81	6	4	–778	15.55	0.63
2	6	–790	11.22	0.74	6	6	–780	9.82	0.77
2	10	–779	8.4	0.80	6	10	–768	28.72	0.32

4. Conclusions

For concluding remarks it can be emphasised that sodium gluconate acts predominately as anodic inhibitor in 3.5% NaCl on carbon steel. Opposite to sodium gluconate, ATMP acts predominately as cathodic inhibitor in 3.5% NaCl. Its optimal concentration for carbon steel RSt 37-2 was 2 mM. By supplementation with sodium gluconate inhibitory effect was further improved. The mixtures of ATMP and sodium gluconate acted predominately as cathodic inhibitors. Although almost all mixtures decreased corrosion current significantly, combinations of moderate concentrations were more successful. Depending on the medium composition ATMP and SG mixtures can act in synergistic or antagonistic manner. This denotes the importance of inhibitory medium optimization. Optimal concentration determined in this work was 2 mM of SG and 2 mM of ATMP. That combination reached efficiency of 84% without any signs of general or pitting corrosion after measurement.

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