Influence of organic/inorganic inhibitors on AISI 304 (1.4301) and AISI 314 (1.4841) steels corrosion kinetics in nitric acid solution

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Abstract: This study evaluates the effectiveness of $KMnO_4$, MK3 and 1-butanol inhibitors on corrosion of AISI 314 and AISI 304 stainless steels using linear and potentiodynamic polarization in 0.1 M HNO_3. The metrics like corrosion potential (E_{corr}), current density (j_{corr}) and polarization resistance (R_p) influence the inhibitor efficacy. The inhibitors improved electrochemical parameters significantly, indicating strong anti-corrosive properties. 1-Butanol had the strongest effect, enhancing corrosion potential and drastically reducing corrosion current density, demonstrating superior protection. The results indicated that without inhibitors, both steels showed higher corrosion rates and more negative potentials, reflecting their susceptibility to corrosion. The introduction of inhibitors markedly improved these parameters, particularly with 1-butanol, which significantly enhanced the polarization resistance and shifted the corrosion potential towards less negative values. The potentiodynamic results highlighted the dynamic effectiveness of inhibitors, reinforcing their role in mitigating corrosion under varied conditions. The study underscores the importance of selecting the appropriate inhibitors to enhance the durability and longevity of stainless steels in acidic environments, with 1-butanol showing the potential for industrial applications requiring high corrosion resistance. This necessitates comprehensive testing to accurately measure inhibitor capabilities in different conditions.

Keywords: austenitic stainless steel; corrosion; inhibitor; linear polarization; potentiodynamic polarization.

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INTRODUCTION

Stainless steels are fundamental to a broad spectrum of industries due to their intrinsic corrosion resistance and mechanical robustness.[1,2] These alloys are categorized into various families: austenitic, ferritic, martensitic and duplex. Among these, the austenitic stainless steels like AISI 304 and AISI 314 are renowned for their formability and resistance to a wide range of environmental conditions.[3,4] The selection of stainless steel for specific applications critically depends on its corrosion resistance. Laboratory tests and/or experiential data assist in selecting suitable steel for use under specific conditions. Alongside choosing the right corrosive medium and test conditions such as pH and temperature, the factors like electrode potential and current density significantly influence corrosion rate. For the testing of pitting corrosion, it is crucial to determine the conditions under which pits form, the critical temperature at which they occur and conditions that lead to the cessation of their growth.[5–8]

Austenitic stainless steel is one of the most commonly used materials in various sectors including construction and industries such as chemical and metallurgy, attributed to its excellent weldability, high-temperature resistance and corrosion resistance. The corrosion resistance of austenitic stainless steel, such as AISI 304 (1.4301) and AISI 314 (1.4841), primarily arises from the rapid formation of a passive film, composed of iron and chromium oxides mixed with hydroxides and water. This film forms instantaneously on the steel surface and has been extensively studied using surface analysis techniques. Corrosion remains a pervasive issue today, posing a continuous challenge for engineers aiming to extend the service life of equipment and enhance operational efficiency. However, the losses due to corrosion are not just limited to replacing corroded parts but also result in significant indirect costs such as downtime, product contamination and enduring environmental damage.[9,10] AISI 304 is particularly valued for its performance in diverse atmospheric and corrosive media, though it is susceptible to corrosion under certain acidic conditions.[11] AISI 314 is noted for its high temperature strength and the resistance to oxidation, requiring specific protective measures in harsh environments.[12]

Stainless steel is not stable in many corrosive environments, necessitating the application of protective measures to extend the lifespan of steel installations. Corrosion inhibitors, in very small concentrations, can reduce the corrosion rates to the technologically acceptable levels, making their use increasingly widespread. Moreover, they are often readily available and cost-effective. Inhibitors can be organic or inorganic and they can provide varying types of protection depending on the environmental conditions.[13] The interaction of these steels with their environments, particularly under the influence of various corrosion inhibitors, has been a significant focus of research. The inhibitors play a crucial role by forming a protective film that reduces corrosion rates significantly. Organic inhibitors,

such as imidazolines and their derivatives, as well as inorganic inhibitors, including phosphates and molybdates, have shown varied effectiveness in protecting these steels in acidic and neutral solutions.[14,15] The effectiveness of such inhibitors is often dependent on their ability to adsorb onto the metal surface and block corrosive agents, a phenomenon thoroughly analyzed in recent studies.[16]

Today, stainless steel is one of the most frequently used materials across all industries due to its excellent properties. It is an alloy material consisting of at least 10.5 % chromium and a maximum of 1.2 % carbon. Austenitic steels are used in a variety of areas, from load-bearing structures and architectural applications to kitchen appliances and medical equipment, not only because of their corrosion resistance but also due to their excellent formability, weldability, durability, *etc*. Some austenitic steels with a high content of alloying elements can withstand temperatures up to 1000 °C. The most well-known (basic) austenitic stainless steel is AISI 304 or 18/8, an iron-based alloy containing nominally 18 % Cr and 8.5 % Ni, including small amounts of C, N, Mn and Si.[17] The corrosion resistance of chromium–nickel steels is based on the presence of a sufficient amount of chromium, which facilitates easy passivation of the metal surface through the formation of adsorptive or phase oxide films of trivalent chromium, thereby bringing iron atoms into a passive state. Despite their resistance, stainless chromium–nickel steels can corrode under certain conditions in specific ways. The most common types of corrosion in stainless steels, in electrolyte solutions, include pitting corrosion, intergranular corrosion, contact corrosion and stress corrosion.[18,19]

Various corrosion inhibitors are added depending on the environment to reduce the rate at which the steel layer is damaged. In acidic environments, corrosion inhibitors such as organic compounds containing nitrogen, sulphur and oxygen and their derivatives are most effective, as they create an organic layer on the metal surface. In neutral environments, nitrites, chromates and permanganates are commonly used. The choice of inhibitors depends on several factors, including cost, availability and environmental impacts.[20,21] Schiff bases have emerged as effective organic inhibitors for AISI 304 and AISI 314 stainless steels, characterized by their ability to form complex films on the steel surface. These compounds show promising inhibition performance in both acidic and neutral environments due to their strong adsorption, facilitated by π-electrons and heteroatoms capable of coordinating with metal atoms on the steel surface.[22,23]

Anodic corrosion inhibitors are often oxidizing agents such as nitrates and nitrites, inorganic ions like chromate, permanganate, molybdate, phosphate and metal ions with higher oxidation numbers: Cu^{+2}, Fe^{+3} and in some cases hydrogen peroxide and oxygen. Although the redox potentials of nitrates and nitrites are close in value, nitrites are shown to be more effective steel inhibitors. The ability of inhibitors to passivize metal and affect the corrosion process depends on

the size of the exchange current density. If the exchange current density is larger, the overpotential of the electrode reactions is small and vice versa.[24] The use of inorganic anodic inhibitors like nitrates and chromates has been critically reassessed due to their environmental impact, prompting research into safer alternatives.[25]

Potassium permanganate is one of the inhibitors commonly used as a "green" corrosion inhibitor.[24] Economically, it is very important that inhibitors act even at low concentrations. Usually, it is sought that Ni be 80–90 %, corresponding to a retardation factor between 5 and 50, *i.e.*, the inhibitor slows down the corrosion process that many times. The effectiveness of corrosion inhibitors depends on many factors, including the type of metal, metal surface, composition and concentration of the corrosive medium, its pH value and temperature and the type and concentration of the inhibitor. Most inhibitors are specific in their action on a particular metal. An inhibitor effective for a certain type of metal may not act on another type of metal or may even have a negative impact.[23]

Furthermore, the development of environmentally benign corrosion inhibitors, such as green inhibitors derived from natural sources like plant extracts, has accelerated. These inhibitors offer sustainable corrosion protection without the adverse environmental impacts associated with traditional inhibitors.[26,27] Recent studies have further elucidated the corrosion mechanisms and inhibition strategies in AISI 304 and AISI 314 steels. For instance, research by Šćepanović *et al.* highlights novel methodologies in the development and application of corrosion inhibitors.[28] Additionally, the work by Stanić *et al.* and Tomić *et al.* provides insights into the synergistic effects of various inhibitors and their interactions with metal surfaces, showcasing the potential for enhancement of the protective outcomes through innovative approaches and advanced analytical techniques.[29,30]

In the current study, corrosion assessments were performed on AISI 304 and AISI 314 steels, conducted under ambient conditions and utilizing one inorganic and two organic inhibitors, all within a 0.1 M HNO_3 solution. This investigation relied on the potentiodynamic polarization and linear polarization methodologies for the evaluation of corrosion behavior. The aim was to deepen the understanding of corrosion processes and inhibitor efficacy for AISI 304 and AISI 314 stainless steels in this manuscript, contributing to the development of more effective corrosion management strategies. By integrating empirical data with theoretical models, the research presented here seeks to provide comprehensive insights into optimizing corrosion inhibition practices to ensure the sustainability and durability of these critical materials in diverse environments.

EXPERIMENTAL

The experimental phase was conducted in the laboratories of the Faculty of Metallurgy and Technology in Podgorica, in collaboration with the Institute of Ferrous Metallurgy in Nikšić. The steel specimens used in this study were procured from the laboratory facilities of

the Institute of Ferrous Metallurgy in Nikšić. The prepared batches of steel underwent a melting process in a 120 kg capacity induction furnace. Each melting cycle, including the alloying process, lasted approximately 150 min per steel variant. The specimens of AISI 304 and AISI 314 steel were produced according to the standardized procedures outlined in ASTM A743 for corrosion--resistant steel castings. This standard specifies rigorous guidelines for melting, casting and cooling processes to ensure high-quality, homogenous austenitic stainless-steel production. The Institute of Ferrous Metallurgy in Nikšić applied a controlled induction melting and alloying process which adheres to this specification. After melting, the steel was cast into quartz sand molds with a silicate binder based on water glass ("Sigel"), with solidification facilitated by CO_2 gas purging to optimize cooling rates and microstructural properties.

The cooling rate was meticulously controlled to promote fine grain structure, enhancing the mechanical properties and corrosion resistance of the steel. This methodically controlled process ensures that the microstructure and grain size of the steel are comparable to comercially available alloys, which is crucial for maintaining the consistency and reliability of our experimental results. Detailed microstructural analysis and comparisons with comercially available AISI 304 and AISI 314 steel variants will be provided to confirm the homogeneity and quality of the manufactured specimens. Subsequent to verification of the chemical composition *via* a quantometer, the molten steel was cast into molds that had been previously prepared. Details regarding the chemical composition of the obtained steel specimens are documented in Table I.

TABLE I. Chemical composition of the AISI 314 and AISI 304 steels utilized in this study

Steel designation	C	Si	Mn	P	S	Cr	Ni	Al	Cu	Mo
AISI 314	0.22	1.57	1.03	0.019	0.012	19.01	17.20	0.06	0.14	0.48
AISI 304	0.05	1.67	0.83	0.015	0.005	17.03	11.53	0.06	0.11	0.12

For the corrosion tests, cylindrical samples with a diameter of 15 mm and a thickness of 5 mm were prepared and utilized as working electrodes. The corrosion tests were conducted using working solutions with specific inhibitor concentrations. The corrosion behavior of AISI 314 and AISI 304 steels was examined in a 0.1 M nitric acid (HNO_3) solution. The influence of inhibitors was also studied in the same solution. A freshly prepared solution was used for each experiment, prepared as follows: 0.1 M HNO_3, obtained by diluting concentrated 65 % HNO_3 with a density of 1.4 g cm^{-3} and a molar mass of 63 g mol^{-1} in distilled water. The inhibitor concentration used was 10^{-4} mol dm^{-3}. All inhibitors were obtained by dissolving measured amounts of high-purity solid substances in distilled water. Shiff bases were not soluble in distilled water, so their solutions were prepared in 96 % ethanol.

In the experiment, $KMnO_4$ was used as an inorganic inhibitor, while Shiff base MK3, (2*E*)-*N*'-[(1*E*)-1-(2-hydroxyphenyl)ethylidene]-2-[1-(2-hydroxyphenyl)ethylidene]hydrazine--1-thiocarbohydrazide and 1-butanol were used as organic inhibitors. All used chemicals were acquired from Sigma Aldrich.

The obtained steels were initially subjected to electrochemical methods of testing (potentiodynamic polarization and linear polarization) in solutions without the presence of inhibitors. Subsequently, testing was performed in the presence of the selected inhibitors. In order to ensure the reliability and reproducibility of our results, all experiments were conducted in triplicate. This approach allowed us to systematically verify the consistency of our findings across multiple trials. The data presented in this study are the average values derived from these replicates, accompanied by standard deviations to reflect the variability observed. Such

statistical treatment provides a robust basis for evaluating the experimental outcomes and supports the reliability of the conclusions drawn from this research.

METHODS

Electrochemical methods

Electrochemical measurements were conducted using a stationary working electrode made from steel samples in a three-electrode thermally controlled electrochemical cell. The exposed surface area of the working electrode was 1 cm^2, so the current values directly represented the corrosion current density. Two graphite electrodes were used as counter electrodes, positioned opposite each other and opposite the working electrode to create a symmetrical electric field. A saturated calomel electrode (SCE) was used as the reference electrode and was in contact with the working electrode through a Luggin capillary. Before each measurement, the steel electrodes were cleaned with P600, P1500, P3000 grit sandpaper and further mechanically polished with alumina pastes of 1, 0.3 and 0.05 μm, successively. Data were acquired using a Princeton Applied Research potentiostat/galvanostat, model 273.

The steel electrode was immersed in the solution, along with the counter and reference electrodes and linear polarization and potentiodynamic polarization measurements were performed. Linear polarization was conducted on the samples of the tested steels, namely polarization ±20 mV relative to the open circuit potential, with a set potential change rate of 0.1 mV s^{-1}, in the specified solutions and using selected inhibitors. Potentiodynamic polarization was performed by continuously changing the potential of the working electrode (1 mV s^{-1}) in both the anodic and cathodic direction. At such polarization values, a region of logarithmic dependence of the net current on the potential of the working electrode (sample) is reached, allowing for the construction of correct Tafel slopes in the log(j)–E coordinate system. The tests were conducted at room temperature, without the introduction of nitrogen, hydrogen or oxygen into the solutions, ensuring that the obtained results corresponded to real systems. The anodic and cathodic polarization curves were obtained for each specimen and the corrosion potentials and corrosion current densities were determined by the Tafel extrapolation and linear polarization methods.

OCP measurements were performed in the aforementioned solutions for 600 s with the data collecting frequency of 2 s^{-1}, or until the potential difference (dE/dt) in the last 5 measurements was smaller than 1 mV h^{-1}, whichever comes first.

RESULTS AND DISCUSSION

Linear polarization

The electrochemical testing of AISI 314 and AISI 304 steels in a 0.1 M HNO$_3$ solution employing both linear and potentiodynamic polarization methods explored the effectiveness of various inhibitors: KMnO$_4$, MK3 and 1-butanol. The measurements included corrosion potential (E_{corr}), corrosion current density (j_{corr}) and polarization resistance (R_p), presented in curves for both methods. For all tested materials, the linear polarization procedure, *i.e.*, polarization ±20 mV with respect to the corrosion potential (E_{corr}), with a set potential change rate of 0.1 mV s^{-1}, was carried out. The results of the corrosion tests for both AISI 314 and AISI 304 steels in 0.1 M HNO$_3$ solution are presented in Fig. 1.
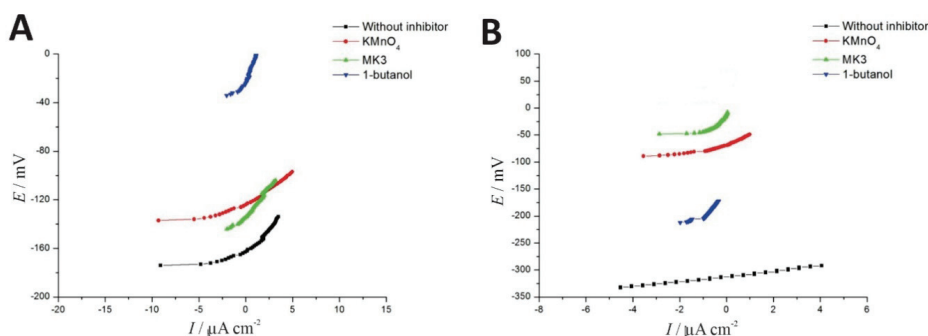
Fig. 1. Potentiodynamic polarization curves for: a) AISI 314 and
b) AISI 304 stainless steels in a 0.1 M HNO$_3$ solution.

The results presented in the research show the corrosion potential ($E(j = 0)$), polarization resistance (R_p) and the corrosion current density (j_{corr}) obtained through linear polarization testing in a 0.1 M HNO$_3$ solution, both with and without the addition of various corrosion inhibitors. The parameters were calculated using Stern–Geary equation. The Stern–Geary equation is given by:

$$I_{corr} = \frac{B}{R_p} \qquad (1)$$

where: I_{corr} is the corrosion current density (A m^{-2}), R_p is the polarization resistance (Ω), B is the Stern–Geary constant, which depends on the electrochemical kinetics of the corroding metal and is typically calculated from:

$$B = \frac{2.303RT}{nF}\left(\frac{b_a b_c}{b_a + b_c}\right) \qquad (2)$$

where R is the universal gas constant (8.314 J mol^{-1}·K^{-1}), T is the temperature (K), n is the number of electrons transferred in the corrosion reaction, F is the Faraday constant (96485 C mol^{-1}), b_a and b_c re the Tafel slopes for the anodic and cathodic reactions, respectively.

The Stern–Geary constant, B, typically ranges between 0.026 and 0.12 V depending on the system and it can also be empirically determined. In our case, it is 0.0217. The parameters offer insights into the anti-corrosive properties conferred by the inhibitors. For AISI 314 without any inhibitor, the corrosion potential was measured at –159 mV, with a polarization resistance of 3.20 kΩ and a corrosion current density of 6.79 µA cm^{-2}. These baselines suggest a moderate level of inherent corrosion resistance. The introduction of KMnO$_4$ as an inhibitor improved the corrosion potential to –124 mV, increased the polarization resistance to 5.08 kΩ and reduced the corrosion current density to 4.27 µA cm^{-2}, indicating a beneficial effect of this inhibitor. The inhibitor MK3 further enhanced these metrics, showing a corrosion potential of –132 mV, an R_p of 7.78 kΩ and j_{corr} of

2.79 µA cm^{-2}. The most substantial improvement was observed with 1-butanol, which altered the corrosion potential dramatically to –5 mV, significantly increased R_p to 21.8 kΩ and lowered j_{corr} to 1.00 µA cm^{-2}, underscoring its superior efficacy.

Similarly, AISI 304 steel displayed a baseline corrosion potential of –324 mV, R_p of 6.12 kΩ and j_{corr} of 3.55 µA cm^{-2} without inhibitors. Upon the application of KMnO$_4$, the corrosion potential improved markedly to –67 mV, with R_p increasing to 16.5 kΩ and j_{corr} decreasing to 1.32 µA cm^{-2}. The inhibitor MK3 produced even more pronounced effects, optimizing the corrosion potential to –50 mV, elevating R_p to 48.1 kΩ and minimizing j_{corr} to 0.45 µA cm^{-2}. 1-Butanol again proved to be the most effective, enhancing the corrosion potential to –155 mV, boosting R_p to 51.6 kΩ and reducing j_{corr} to 0.42 µA cm^{-2}. The inhibitors did not only increase the polarization resistance but also shifted the corrosion potential towards less negative values and markedly decreased the corrosion current density. Among the tested inhibitors, 1-butanol emerged as the most effective, demonstrating exceptional enhancement of corrosion resistance parameters across both types of stainless steel. This suggests that careful selection of inhibitors is crucial for the applications where these steels may encounter corrosive environments, particularly in acidic conditions like those simulated with HNO$_3$.

Fig. 1 shows the polarization curves recorded within a low polarization region and corrosion potential and the corrosion current density are determined from these plots. It provides insights into each inhibitor's capacity to mitigate corrosion. For AISI 314, the control condition exhibits a corrosion potential of –159 mV and a current density indicative of significant corrosion activity. The addition of KMnO$_4$ improves the corrosion potential to –124 mV and reduces the current density, suggesting an enhancement in corrosion resistance. MK3 offers further improvement, achieving a more positive potential of –132 mV and a lower current density. The most profound impact is observed with 1-butanol, which shifts the corrosion potential significantly to –25 mV and minimizes the current density, highlighting its superior effectiveness in enhancing corrosion resistance. In the case of AISI 304, the absence of inhibitors results in a highly negative corrosion potential of –324 mV and a moderate current density. The application of KMnO$_4$ improve these parameters to –67 mV, indicating effective corrosion protection. MK3 further enhances these effects, with a potential of –50 mV and a reduced current density. However, 1-butanol demonstrates the greatest efficacy, substantially increasing the potential to –155 mV and achieving the lowest current density among the tested conditions, signifying exceptional corrosion protection. It can be stated that all tested inhibitors significantly improve the corrosion resistance of both AISI 314 and AISI 304 steels. The effectiveness of 1-butanol, in particular, stands out, markedly shifting the corrosion potential towards less negative values and drastically reducing the corrosion current density. The relation

between the graphical and tabular data for both AISI 314 and AISI 304 stainless steels underlines the effectiveness of the corrosion inhibitors tested. Fig. 1 representations align well with the quantitative data, illustrating not only the efficacy of each inhibitor but also highlighting the comparative performance between the two steel types. The results from Fig. 1 underline the substantial improvements in corrosion resistance brought about by the inhibitors, with 1-butanol standing out as the most effective in enhancing the material's durability against corrosive environments. This implies a strong passivation effect, likely due to the formation of a protective barrier on the steel surface, which is crucial for applications where these materials are exposed to corrosive environments. The results underscore the importance of selecting appropriate corrosion inhibitors to enhance the longevity and durability of stainless steels in acidic conditions.

OCP measurements

Fig. 2 shows the open circuit potential (OCP) traces over time, illustrating the stabilization effect of corrosion inhibitors $KMnO_4$, MK3 and 1-butanol compared to uninhibited conditions in a 0.1 M HNO_3 solution.
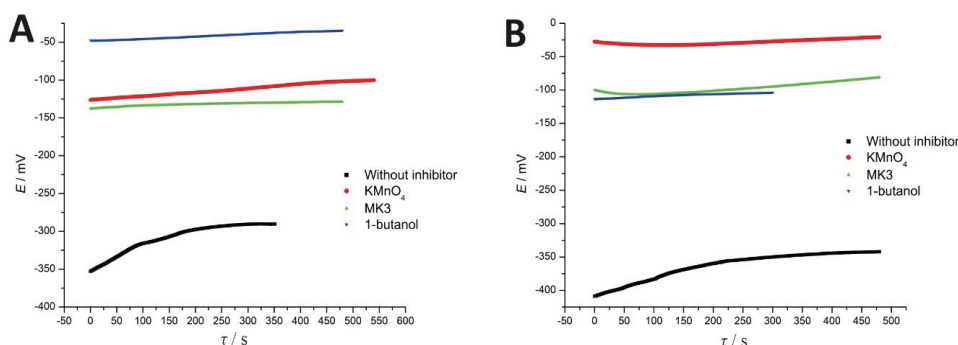

Fig. 2. Open circuit potential (OCP) traces for: a) AISI 314 and
b) AISI 304 stainless steels in a 0.1 M HNO_3 solution.

The open circuit potential (OCP) traces for AISI 314 and AISI 304 stainless steels in a 0.1 M HNO_3 solution are depicted over a 500 s interval. These traces were recorded to evaluate the stability of the electrochemical systems under various conditions, including the application of three different corrosion inhibitors: $KMnO_4$, MK3 and 1-butanol, compared to the uninhibited systems.

For AISI 314, the OCP trace without any inhibitor exhibits a notable downward trend, suggesting a continuous increase in corrosion activity over time. This observation indicates an unstable electrochemical system where the steel surface is actively corroding. Conversely, the introduction of corrosion inhibitors significantly alters this behavior. $KMnO_4$ and MK3 both stabilize the potential after initial fluctuations, with $KMnO_4$ maintaining a relatively constant potential

around –150 mV and MK3 around –100 mV, indicating effective surface passivation and reduced corrosion rates. Notably, 1-butanol shows the most effective inhibition, with the OCP trace remaining stable and closest to zero potential, suggesting minimal corrosion activity and enhanced system stability. Similarly, the OCP traces for AISI 304 reflect comparable trends. The uninhibited condition again shows a progressive decrease in potential, demonstrating the current corrosion. The application of $KMnO_4$ results in a stabilized potential, though it does not achieve the level of stability observed with MK3 or 1-butanol. MK3 provides a stable potential around –100 mV, similar to its effect on AISI 314. In contrast, 1-butanol exhibits superior performance with the most stable and least negative potential among the conditions tested, indicating the robust corrosion protection and the most stable electrochemical system among the configurations tested.

These observations underline the effectiveness of the corrosion inhibitors in stabilizing the electrochemical characteristics of AISI 314 and AISI 304 stainless steels in corrosive environments. The results demonstrate that while all inhibitors improve stability compared to the uninhibited systems, 1-butanol consistently shows the highest efficacy in maintaining near-neutral potentials, thereby providing the best protection against corrosion. This behavior suggests that 1-butanol may form a more comprehensive and protective barrier on the metal surface, which is crucial for applications where these materials are exposed to corrosive conditions.

Potentiodynamic polarization

The corrosion parameters are obtained from the polarization curves for AISI 314 and AISI 304 steels, which are presented in Fig. 3.
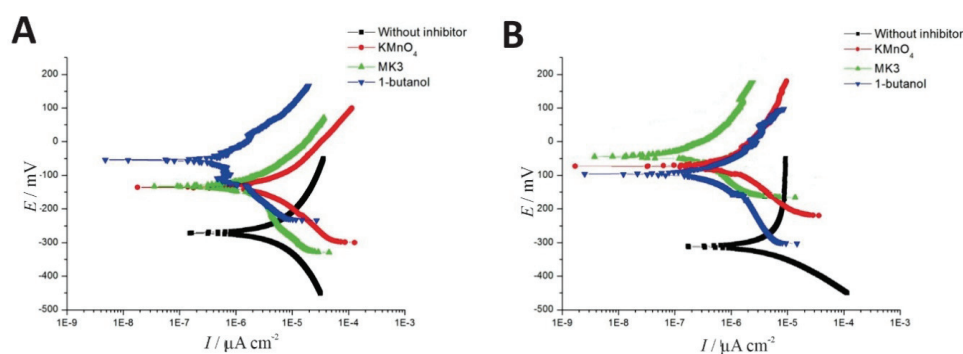

Fig. 3. Detailed potentiodynamic polarization responses of: a) AISI 314 and b) AISI 304 stainless steels.

Detailed insights from potentiodynamic polarization tests conducted on AISI 314 and AISI 304 stainless steels in a 0.1 M HNO_3 solution, assessing the effectiveness of various corrosion inhibitors including $KMnO_4$, MK3 and 1-butanol are shown in the forthcoming text. The parameters evaluated in this study include

open circuit potential (OCP), corrosion potential ($E(j = 0)$), anodic Tafel slope (b_a), cathodic Tafel slope (b_c) and corrosion current density (j_{corr}).

For AISI 314, the results indicate a substantial improvement in corrosion resistance upon the application of inhibitors. Without any inhibitor, the steel exhibits an OCP of –290 mV and a corrosion potential of –272 mV, with relatively high Tafel slopes (878 mV dec^{-1} for b_a and –724 mV dec^{-1} for b_c) and a corrosion current density of 27.85 µA cm^{-2}, suggesting a higher corrosion rate. The introduction of KMnO$_4$ shifts the OCP to –100 mV and the corrosion potential to –136 mV, significantly lowering the Tafel slopes to 183 mV dec^{-1} for b_a and –181 mV dec^{-1} for b_c and reducing the corrosion current density to 6.13 µA cm^{-2}. This denotes a significant improvement in corrosion resistance. MK3 further enhances these effects, evidenced by an even lower corrosion current density of 3.49 µA cm^{-2}, despite the OCP and $E(j = 0)$ being relatively close (–129 and –133 mV, respectively), with Tafel slopes of 190 mV dec^{-1} for b_a and –328 mV dec^{-1} for b_c. The application of 1-butanol shows the most significant enhancement, with the lowest corrosion current density of 0.58 µA cm^{-2} and Tafel slopes of 136 mV dec^{-1} and –174 mV dec^{-1}, suggesting highly effective corrosion inhibition.

Similarly, for AISI 304, the use of inhibitors demonstrates a profound effect on corrosion characteristics. The uninhibited condition shows an OCP of –342 mV, a corrosion potential of –324 mV and a higher corrosion rate indicated by a j_{corr} of 8.88 µA cm^{-2}. KMnO$_4$ substantially improves the parameters with an OCP of –20 mV and a corrosion potential of –73 mV, along with a reduced j_{corr} of 1.68 µA cm^{-2}. MK3, displaying the best results among the inhibitors tested for AISI 304, significantly lowers the corrosion current density to 0.39 µA cm^{-2}, with an OCP of –81 mV and a remarkably improved corrosion potential of –27 mV. However, despite 1-butanol reducing the j_{corr} to 1.16 µA cm^{-2}, it results in a slightly more negative corrosion potential (–96 mV) compared to KMnO$_4$ and MK3, with an unexpectedly higher OCP of –103 mV. Tafel slopes for different inhibitors for AISI304 are given in Table II.

TABLE II. Tafel slopes for different corrosion inhibitors in 0.1 M HNO$_3$ solution for AISI304

Inhibitor	b_a / mV dec^{-1}	b_c / mV dec^{-1}
No inhibitor	412	–186
KMnO$_4$	321	–150
MK3	263	–125
1-Butanol	243	–293

The collective results from both AISI 314 and AISI 304 stainless steels confirm that the tested inhibitors significantly mitigate corrosion processes in a nitric acid environment. The differences in Tafel slopes and corrosion potentials across different inhibitors reflect the variance in their mechanisms and efficiencies at protecting the steel substrates. Particularly notable is the effectiveness of MK3 and

1-butanol, which does not only lower j_{corr} but also substantially adjust the electrochemical parameters towards more favorable values, thus enhancing the corrosion resistance of both steel types under these challenging conditions.

The presented data emphasize two crucial electrochemical parameters, OCP and $E(j = 0)$. Understanding the differences between these parameters can shed light on the inhibitor's impact on the electrochemical behavior of these steels. OCP is the potential of the electrochemical cell when no external current is applied and it reflects the natural thermodynamic equilibrium state of the electrode in its environment. This measurement is passive and indicates the inherent stability of the metal surface in the solution. $E(j = 0)$, on the other hand, is derived from active polarization tests. It is typically obtained through Tafel extrapolation, where the intersection of the anodic and cathodic Tafel slopes is computed. This value represents the potential at which the net anodic and cathodic currents balance each other out, indicating the potential at which the corrosion rate (current density, j_{corr}) is minimal.

For the uninhibited condition for AISI 314, the OCP is at –290 mV, whereas $E(j = 0)$ is slightly more positive at –272 mV. The difference suggests that upon applying an external potential, the electrochemical reactions tend to stabilize at a slightly more noble potential. With inhibitors like $KMnO_4$, MK3 and 1-butanol, the OCP and $E(j = 0)$ values become closer. For example, with 1-butanol, OCP is –34 mV and $E(j = 0)$ is –56 mV, indicating a more effective stabilization of the surface, likely due to the formation of a protective layer that reduces active sites for corrosion. AISI 304 Steel: without inhibitors, the OCP is –342 mV and $E(j = 0)$ is –324 mV. This again indicates a stabilization at a more noble potential when polarization begins. The use of inhibitors reduces the gap between OCP and $E(j = 0)$. Particularly, with MK3, OCP is –81 mV and $E(j = 0)$ is –27 mV. This significant shift towards less negative values indicates a strong inhibition effect, possibly due to the formation of a dense protective film. The difference between OCP and $E(j = 0)$ across different inhibitors and conditions suggests varying degrees of influence by the inhibitors on the electrochemical properties of the steel. A smaller difference typically indicates a more effective inhibition, as the steel's surface characteristics under passive and active conditions become more similar, reflecting a stable and protective inhibitor film. These observations align with corrosion science principles suggesting that effective inhibitors either passivize the metal surface or alter the kinetics of anodic and cathodic reactions to reduce overall corrosion rates. The closer alignment of OCP and $E(j = 0)$ under inhibitor-treated conditions confirms the establishment of a more homogenous and less reactive surface state.

These graphs in Fig. 3 are essential for understanding the electrochemical behavior of AISI 304 and AISI 314 stainless steels under corrosive conditions and evaluating the efficacy of the inhibitors. For AISI 314, the polarization curve

without an inhibitor shows a significantly negative corrosion potential and high current density, indicating a high rate of corrosion susceptibility. The introduction of $KMnO_4$ results in a noticeable shift towards a less negative potential and reduced current density, though it is less effective compared to the other inhibitors. MK3 demonstrates a further improvement, significantly reducing the current density and mildly improving the potential. The most pronounced effect is observed with 1-butanol, which not only shifts the potential towards less negative values but also drastically lowers the current density, suggesting a highly effective inhibition of corrosion. Similarly, the AISI 304 steel exhibits even more dramatic shifts in electrochemical behavior with the application of inhibitors. Without any inhibitor, the steel displays the most negative potential and relatively high current density, indicative of considerable corrosion activity. With $KMnO_4$, the potential is moderately less negative and the current density is notably decreased. MK3 shows a substantial decrease in current density and shifts the potential to less negative values, marking it as highly effective. However, 1-butanol stands out by further reducing the current density significantly, although its impact on shifting the potential is not as pronounced as with MK3.

These observations suggest that the inhibitors tested significantly enhance the corrosion resistance of both AISI 314 and AISI 304 steels in nitric acid environments. The shift in potential towards less negative values and the reduction in j_{corr} across the inhibitors indicate their effectiveness, with 1-butanol and MK3 showing particularly strong performance in reducing the electrochemical signs of corrosion. This implies that these inhibitors likely form protective barriers or passivize the surface, effectively reducing the electrochemical reactions that lead to corrosion. The results highlight the importance of selecting appropriate corrosion inhibitors to extend the service life of stainless steels in corrosive environments.

To address the discrepancies between the $E(j = 0)$ values reported in the manuscript for the linear and potentiodynamic polarization tests, it is important to consider the intrinsic differences in the methodologies and how they interact with the electrochemical properties of AISI 314 and AISI 304 steels in a 0.1 M HNO_3 solution. The variations in these values are not indicative of experimental errors or instability in the system, but rather reflect the fundamental differences between the methods and their impacts on the electrode surface. Linear polarization provides a more conservative estimate of the corrosion potential because it involves small perturbations around the open circuit potential. This method is less likely to disrupt the native oxide layer or any inhibitor-induced film on the metal surface, thus providing a value of $E(j = 0)$ that reflects a minimally disturbed state. In linear polarization, $E(j = 0)$ is closer to the real corrosion potential under near-static conditions and thus is likely a better representation of the material's behavior in less aggressive environments. The potentiodynamic polarization involves a dynamic sweep of the potential that can extend well beyond the passive

range into the active corrosion or transpassive regions. This sweep can modify surface conditions, such as through the stripping away of passive layers or the enhanced formation of corrosion products, leading to different apparent $E(j = 0)$ values. In potentiodynamic tests, $E(j = 0)$ is extrapolated from the Tafel slopes, where the intersections represent a theoretical balance between anodic and cathodic currents. This method inherently assumes uniformity in reaction kinetics across the swept range, which might not hold in environments where inhibitor films are forming or being compromised. The findings from both tests are valid within the scope of their respective methodologies. The variance in $E(j = 0)$ values in the tests highlights the importance of selecting the appropriate testing protocol based on the specific service conditions expected for the metal. Furthermore, these results display the complex nature of corrosion processes and the need for multiple approaches to accurately gauge the effectiveness of corrosion inhibitors.

Protection efficiency

The protection efficiency, based on the data, is calculated using the Eq. (3):

$$\eta = \frac{j_{corr} - \left(j_{corr}\right)_{inh}}{j_{corr}} \tag{3}$$

where j_{corr} is the corrosion current density in the uninhibited solution and $(j_{corr})_{inh}$ is in the inhibited solution.

The corrosion inhibition efficiencies derived from linear polarization tests (LP) and potentiodynamic measurements (PD) are summarized in forthcoming paragraphs.

Fig. 4 displays a comparative analysis of corrosion inhibition efficiency for AISI 314 and AISI 304 stainless steels, employing three different inhibitors (KMnO$_4$, MK3, 1-butanol) and utilizing two distinct electrochemical testing methods: linear polarization and potentiodynamic polarization. The bar chart measures the efficiency (η) in percentage terms, indicating how effectively each inhibitor reduces the corrosion rate compared to an uninhibited system.

For AISI 314, the corrosion rates without any inhibitors serve as a baseline, showing a j_{corr} of 6.79 µA cm^{-2} for LP and 27.8 µA cm^{-2} for PD. KMnO$_4$ decreases the corrosion rate to 4.27 µA cm^{-2} in LP, achieving 37.1 % efficiency and to 6.13 µA cm^{-2} in PD with a significantly higher efficiency of 77.9 %. This suggests that KMnO$_4$ inhibition mechanism might be more dynamically effective, as captured by the PD method. MK3 provides an even stronger inhibition, reducing the corrosion rate to 2.79 µA cm^{-2} in LP (58.9 % efficiency) and to 3.488 µA cm^{-2} in PD (87.5% efficiency). 1-Butanol exhibits the highest protection, reducing the corrosion rate dramatically to 1.00 µA cm^{-2} in LP (85.3 % efficiency) and to an

impressive 0.58 µA cm^{-2} in PD (97.9 % efficiency), demonstrating its superior efficacy in both static and dynamic conditions.
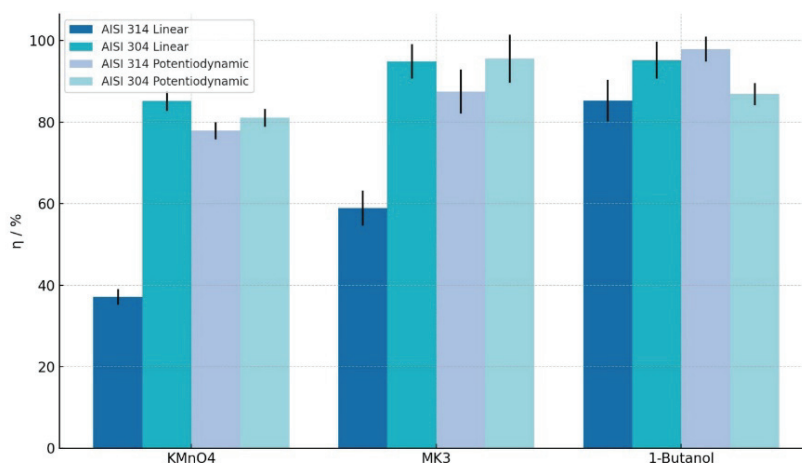

Fig. 4. Overall corrosion inhibition efficiency performance comparison.

Turning to AISI 304, the initial corrosion rates are lower, with 3.55 µA cm^{-2} in LP and 8.88 µA cm^{-2} in PD. With KMnO$_4$, the corrosion rate is reduced to 1.32 µA cm^{-2} in LP, achieving an 85.2 % efficiency and slightly less effectively in PD to 1.68 µA cm^{-2} (81.1 % efficiency). MK3 again performs excellently, lowering the corrosion rate to 0.45 µA cm^{-2} in LP (94.9 % efficiency) and to 0.39 µA cm^{-2} in PD (95.6 % efficiency), showing minimal variation between methods. 1-Butanol also shows strong performance, reducing corrosion to 0.42 µA cm^{-2} in LP (95.2 % efficiency) and to 1.16 µA cm^{-2} in PD (86.9 % efficiency), which suggests a slight decrease in effectiveness under dynamic testing conditions for this inhibitor on AISI 304 compared to AISI 314.

These observations highlight that the choice of the corrosion inhibitor and the method of testing are both crucial in evaluating their effectiveness. 1-Butanol and MK3 consistently show high efficiencies across both types of steel and methods, suggesting their robust performance in various conditions. KMnO$_4$, while generally effective, shows some variability in performance, especially under different testing dynamics. The results emphasize the importance of selecting an inhibitor based on specific environmental conditions and the type of stainless steel, ensuring optimal protection against corrosion. This comprehensive analysis also underscores the value of using multiple testing methods to accurately gauge inhibitor performance across different operational scenarios. Interestingly, the potentiodynamic method tends to show slightly higher efficiencies for AISI 314, particularly noticeable with MK3. This might be due to the dynamic nature of this method, which show more about the protective film formation dynamics, or other

interactive effects at the metal-solution interface that are not as apparent in linear polarization tests.

In the linear polarization tests, AISI 314 steel exhibited a notable shift towards less negative corrosion potentials and a reduction in corrosion current with the application of 1-butanol, highlighting its potent protective capabilities. This shift is indicative of a strong adsorptive interaction between the inhibitor and the steel surface, potentially leading to the formation of a dense molecular barrier that impedes corrosive interactions at the metal–solution interface, as detailed in Fig. 1. For AISI 304 steel, the application of $KMnO_4$ and the Schiff base MK3 resulted in significant improvements in corrosion potential, as shown in Fig. 3. The effectiveness of $KMnO_4$ can be attributed to its ability to oxidize the steel surface, thereby forming a protective oxide layer. In contrast, MK3, being a Schiff base, operates through a different mechanism. Schiff bases are known for their ability to form stable complexes with metal ions due to their conjugated system and the presence of nitrogen and sulphur donor atoms. These complexes can effectively passivize the surface, blocking both the anodic and cathodic sites necessary for corrosion reactions.

Potentiodynamic testing further supported these findings, where 1-butanol demonstrated a substantial reduction in both corrosion rate and potential deviation for both steel types, indicative of its strong protective properties. The corrosion inhibition efficiencies show the varied effectiveness of these inhibitors, highlighting how the structural features and reactive sites of inhibitors like MK3 contribute to their mode of action. $KMnO_4$ typically enhances the formation of an oxide layer, while MK3, through its Schiff base structure, forms chelates with metal ions at the surface, providing a robust shield against corrosion.

CONCLUSION

The comprehensive analysis of the electrochemical testing conducted on AISI 314 and AISI 304 steels using linear and potentiodynamic polarization methods highlights the significant impact of corrosion inhibitors $KMnO_4$, MK3 and 1-butanol in a 0.1 M HNO_3 solution. The investigation employed detailed measurements including corrosion potential (E_{corr}), corrosion current density (j_{corr}) and polarization resistance (R_p), which were crucial for assessing the inhibitors' effectiveness. Based on all the conducted research in this experimental work, the following conclusions can be drawn:

•   The linear polarization results for both steel types indicate that without inhibitors, the steels are naturally prone to corrosion in nitric acid environments, as evidenced by their relatively high corrosion current densities and negative corrosion potentials. However, the addition of inhibitors has markedly improved these parameters. $KMnO_4$, while offering moderate improvement, is overshadowed by the more significant enhancements brought about by MK3 and

especially 1-butanol, which did not only reduce the corrosion current density but also dramatically shifted the corrosion potential towards less negative values. For AISI 314, 1-butanol was particularly effective, enhancing the corrosion potential by over 130 mV compared to the uninhibited condition and significantly boosting the polarization resistance.

• Similarly, AISI 304 showed a notable response to the inhibitors. The application of KMnO$_4$ and MK3 resulted in improvement of corrosion potentials and lower corrosion current densities, however, 1-butanol stood out, achieving the most substantial improvement in all parameters measured. This suggests that 1-butanol may be forming a more effective protective barrier on the steel surface, likely through strong adsorptive interactions and possibly the formation of a dense molecular barrier that impedes corrosive reactions.

• The potentiodynamic polarization results further reinforce these findings, showing that the dynamic nature of this method captures the inhibitors' protective mechanisms effectively. The results from both AISI 314 and AISI 304 steels confirm that dynamic conditions may better represent the inhibitors' performance, particularly in how they interact with the steel surfaces by varying electrochemical conditions.

• Schiff base MK3 exhibits very good results and the reason is its chemical structure (C=N bond) and the ability to form a protective monolayer on the steel surface. Changes in the functionality of the group on the terminal aromatic ring led to the changes in the efficiency of inhibition of the corresponding Schiff base compounds. Since synthesized Schiff bases have not been previously used as inhibitors, this experimental work demonstrates their potential application, leaving room for further research and testing on samples of different materials and chemical compositions. Moreover, when analyzing all the obtained results for the efficiency of the inhibitors used in both testing methods (linear and potentiodynamic polarization), 1-butanol has proven to be the most effective inhibitor in the 0.1 M HNO$_3$ solution.

• The consistency between the graphical data and the presented results underscores the efficacy of the testing methods and the reliability of the results. The notable correspondence between the decrease in corrosion rates and the improvement in corrosion potentials across both testing formats highlights the effectiveness of MK3 and 1-butanol in significantly enhancing the corrosion resistance of the steels. The study clearly demonstrates that the selection of an appropriate corrosion inhibitor is crucial for enhancing the durability and longevity of stainless steels in acidic environments. The superior performance of 1-Butanol across both types of stainless steel and both electrochemical testing methods suggests its potential utility in industrial applications where corrosion resistance is paramount. This research does not only provide the valuable insights into the comparative performance of corrosion inhibitors but also highlights the importance of

using multiple testing methods to capture the full range of an inhibitor's protective capabilities in different environmental conditions.

И З В О Д

УТИЦАЈ ОРГАНСКИХ/НЕОРГАНСКИХ ИНХИБИТОРА НА КИНЕТИКУ КОРОЗИЈЕ ЧЕЛИКА AISI 304 (1.4301) И AISI 314 (1.4841) У РАСТВОРУ АЗОТНЕ КИСЕЛИНЕ

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Ова студија процењује ефикасност инхибитора $KMnO_4$, МК3 и 1-бутанола на корозију нерђајућих челика AISI 314 и AISI 304, коришћењем линеарне и потенциодинамичке поларизације у 0,1 M HNO_3. Корозиони потенцијал (E_{corr}), густина струје корозије (j_{corr}) и поларизациони отпор (R_p) су коришћени за процену ефикасност инхибитора. Инхибитори су значајно побољшали електрохемијске параметре, што указује на јака антикорозивна својства. 1-бутанол је имао најизраженији ефекат, повећавајући корозиони потенцијал и драстично смањујући густину струје корозије, показујући врхунску заштиту. Резултати су показали да без инхибитора, оба челика показују већу брзину корозије и негативније корозионе потенцијале, што одражава њихову подложност корозији. Увођење инхибитора је значајно побољшало ове параметре, посебно 1-бутанола, који је значајно повећао отпорност на поларизацију и померио потенцијал корозије ка мање негативним вредностима. Потенциодинамички резултати су истакли динамичку ефикасност инхибитора, појачавајући њихову улогу у ублажавању корозије у различитим условима. Студија наглашава важност одабира одговарајућих инхибитора за побољшање издржљивости и дуговечности нерђајућег челика у киселим срединама, при чему 1-бутанол показује потенцијал за индустријску примену која захтева високу отпорност на корозију. Ово захтева свеобухватно тестирање за прецизно мерење способности инхибитора у различитим условима.

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