Investigation the effects of Na$_2$MoO$_4$ as an inhibitor on electrochemical corrosion behavior of 316L stainless steel in LiBr solution

**ABSTRACT**

The effect of sodium molybdate (Na$_2$MoO$_4$) as an inhibitor at various concentrations of 50, 100 and 200ppm on the electrochemical corrosion behavior of 316L stainless steel in LiBr solution at 60°C was studied by polarization curves, electrochemical impedance spectroscopy (EIS) methods and electron microscopy. Polarization curves indicate that Na$_2$MoO$_4$ acts as mixed-type inhibitor. The corrosion resistance of 316L stainless steel samples increases with the inhibitor concentration up to 200ppm. By increasing the inhibitor concentration from 50ppm to 200ppm, corrosion current density decreases. These results were confirmed by further analysis using a scanning electron microscope.

**Keywords:** sodium molybdate, corrosion, 316L stainless steel, Lithium bromide.

1. INTRODUCTION

Corrosion has been one of the most critical fields of study for many years. Researchers have tried different approaches such as applying coatings or using some specific ceramics because of their high chemical stability [1-5].

However, despite the outstanding corrosion resistivity of ceramics, steel is still one of the most applicable materials in industry. Therefore, it is essential to enhance its corrosion resistivity under severe conditions such as high temperatures in heat exchangers [6-11].

Lithium bromide (LiBr) has been widely used in absorption refrigeration systems due to its favorable thermophysical properties. Circulation of LiBr solution within the pumps and pipes are required during the operation of these systems [12-19]. Although LiBr possesses favorable thermophysical properties, it can cause serious corrosion problems in the metallic components in refrigeration systems and heat exchangers in absorption plants [20-23]. Other disadvantages of the LiBr/water mixtures are:

- a) low working pressure, b) high corrosion rates at high temperatures, and c) tendency to crystallize at high LiBr concentrations. However, there are not data available concerning the corrosion problems caused by LiBr [24, 25].

Generally, stainless steels are not corrosion resistant in aggressive environments and they are prone to local corrosion including pitting corrosion [26, 27]. This form of corrosion is very destructive and dangerous because of the possibility of material perforation. Stainless steels are widely used in absorption systems components such as condensers, evaporators and absorbers due to their high corrosion resistance [28, 29]. Among the different stainless steels, austenitic ones and specially AISI 316L SS are often used for its high corrosion resistance. However, due to factors such as high temperature and LiBr concentration, stainless steels can suffer from severe corrosion problems. For this reason, the expected high corrosion effects of the LiBr aqueous solutions guide us to use corrosion inhibitors added to these environments. However, there exist very few inhibitors, which satisfy both technological and ecological requirements at the same time [30,31]. Normally, inhibitors are used for corrosion control in closed systems. The functionality of some corrosion inhibitors depends on the type of material, its properties and the corrosive environment. Chromate (CrO$_4^{2-}$) is a very effective passivating inhibitor at relatively high levels. It is

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very effective for ferrous alloys in the presence of halide ions. It can passivate metals by forming mono-atomic or polyatomic oxide film on the electrode surface. Thus, chromates are very good inhibitors to prevent pitting corrosion for stainless steels. Nitrites (NO$_2^-$) and molybdates (MoO$_2^-$) are inorganic, passivating inhibitors, which have been used in many corrosive environments. For instance, molybdates have been used to prevent mild steel and cold rolling steel [32,33] corrosion in simulated cooling water, acidic solutions [34, 35]. They can also be used to seal phosphate coatings on hot-dip galvanized steel [36,37] or on the bacterial corrosion or iron [38,39].

In 1953, Robertson first studied the inhibitive effect of MoO$_2^-$ on the corrosion of carbon steel in neutral solution [40]. Afterwards, there are many papers in the literature concerning the application of MoO$_2^-$ as an effective inhibitor for corrosion of steel in neutral or approximate neutral media [41]. Besides steel, magnesium alloy in simulated cooling water have been protected against corrosion using MoO$_2^-$ [42,43].

Table 1. Chemical composition of L316 stainless steel

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
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<tr>
<td></td>
<td>0.03</td>
<td>2</td>
<td>0.75</td>
<td>0.045</td>
<td>0.03</td>
<td>16.5</td>
<td>2.3</td>
<td>10.8</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2. Corrosion rate measurements

2.2.1. Potentiodynamic polarization studies

The corrosion parameters of samples in different concentration of sodium molybdate were studied using potentiodynamic polarization in LiBr solution. The potentiodynamic polarization experiments were conducted by sweeping the potential at a scan rate of 1 mVs$^{-1}$ in the range of -250mV to +500mV versus open circuit potential (OCP) using PARSTAT 2273 advanced electrochemical system (Princeton Applied Research). The results were analyzed via Tafel extrapolation theory. Tafel plots were obtained from the data and the corrosion current density (Icorr) was determined by extrapolating the straight-line section of the anodic and cathodic Tafel lines. In order to have a better comparison between the results obtained by the electrochemical methods, all measurements were carried out in the same conditions. Hence, for all tests, three-electrode set up including working electrode (test samples), platinum auxiliary electrode, and a saturated calomel reference electrode (SCE) were used for the corrosion studies. Before any electrochemical test, the samples were left to stabilize for 30 min. Pitted surfaces of the working electrode AISI 316Ti after potentiodynamic polarization tests were observed by a scanning electron microscope (SEM), TESCAN-XMU model. After potentiodynamic polarization tests in LiBr solution with and without inhibitor addition, the samples were cleaned ultrasonically in alcohol to remove the corrosion products from surface.

2.2.2. Electrochemical impedance spectroscopy (EIS)

In order to better understand the corrosion behavior of samples in terms of corrosion resistance, the impedance spectra were acquired in the frequency range of 100kHz to 10mHz in LiBr solution. The impedance data was modeled using Zview software.

3. RESULTS AND DISCUSSION

3.1. Corrosion measurements

The open circuit potential is a parameter which indicates the tendency of a material to electrochemical oxidation in a corrosive medium based on thermodynamics. This potential may vary with time due to the changes in the nature of the surface of the electrode (oxidation, formation of the passive layer or immunity). In figure 1, open circuit diagrams, shows potential changes with time for solution in the absence and presence of sodium molybdate in different concentration. According to the figure, in the absence of inhibitor, the trend is...
Investigation the effects of Na$_2$MoO$_4$ as an inhibitor on electrochemical properties of stainless steel samples. This indicates that the sample in this case is corroded and the corrosion product is formed on it, which in turn has a higher potential. With the addition of 50ppm Na$_2$MoO$_4$, the initial value of the potential shifted to the higher values, which caused the formation of the protective layer by the absorption of inhibitor on the surface of sample but the changes of the potential values are not stable and show that complete inhibition does not occur. These changes can also be seen in the presence of 100ppm inhibitor. According to figure 1, sample with 200ppm sodium molybdate is the most stable state. In this sample, although the potential is lower than 50ppm and 100ppm but it suggests that by adsorption, corrosion is prevented at the early stages.

Figure 1. Open circuit potential versus time for the 316L stainless steel samples in LiBr solution with various Na$_2$MoO$_4$ concentrations.

Slika 1. Potencijal otvorenog kola u odnosu na vreme za uzorke 316L od nerđajućeg čelika u LiBr rastvoru sa različitim koncentracijama Na$_2$MoO$_4$.

Figure 2 shows the electrochemical results obtained from the polarization studies for 316L stainless steel samples in LiBr solution containing various concentrations of Na$_2$MoO$_4$ at 60°C. The electrochemical corrosion parameters obtained from the polarization curves are summarized in Table 2. According to polarization tests, all three inhibitor concentrations lead to relatively higher corrosion resistivity of samples in the LiBr solution. The presence of the inhibitor shifts the polarization curves to the lower values of current densities [45]. In other words, the stainless steel corrosion is hindered by Na$_2$MoO$_4$. According to the results in Table 2, Na$_2$MoO$_4$ is considered as adsorption inhibitors.

By increasing the concentration of the inhibitor, more anode active sites are covered and also in cathode sites, the hydrogen progression is prevented. In this context, decreasing the corrosion current density is associated with increasing the concentration of inhibitor in the solution and according to Figure 2 and Table 2, the lowest corrosion current density is for 200ppm sodium molybdate. As we can see the higher inhibitor concentration (200ppm) caused the extension of the passive region to higher positive potential values [46]. According to Table 2, the anodic and cathodic slopes have changed and this suggests that sodium molybdate acted as mixed-type inhibitors.

<table>
<thead>
<tr>
<th>Inhibitors Concentration (ppm)</th>
<th>$E_{corr}$ (mv)</th>
<th>$I_{corr}$ (A)</th>
<th>$a$(mv)$\beta$</th>
<th>$b$(mv)$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-194</td>
<td>$9 \times 10^{-6}$</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>50</td>
<td>-192</td>
<td>$2 \times 10^{-6}$</td>
<td>87</td>
<td>64</td>
</tr>
<tr>
<td>100</td>
<td>-101</td>
<td>$5 \times 10^{-7}$</td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td>200</td>
<td>-120</td>
<td>$2 \times 10^{-7}$</td>
<td>99</td>
<td>93</td>
</tr>
</tbody>
</table>
In order to further understand the corrosion behavior, samples were examined by Electrochemical impedance spectroscopy (EIS). Figure 3 represents the Nyquist and Bode’s diagrams for 316L SS in LiBr solution without and with various concentrations of Na$_2$MoO$_4$ at 60°C. The Nyquist plots for all samples exhibit a semicircle shape and the sizes of the loops are different from each other. As it stands, there is one time constant in the absence of sodium molybdate. This time constant is related to the electrical double layer on the surface of the sample indicating that there is a mechanism for corrosion of the substrate. This mechanism is primarily related to the double layer between the metal and solution [47].

In the presence of inhibitor, based on Bode diagrams, there are two time constants, suggesting that this is the surface film, which controls the corrosion reactions. By increasing the charge transfer resistance for this film and by increasing the inhibitor concentration, better protective and compact film is made. The second time constant values can be charge transfer reactions at the interface of the surface film caused by inhibitor and the surface of 316L stainless steel [48].

A more detailed interpretation of the EIS measurements was performed by fitting the experimental plots using equivalent electrical circuit models which were proposed in order to simulate the electrochemical behavior of the studied coatings. These models were based on the combination of resistances, capacitances, and other elements that should have a physical meaning, related to the electrochemical response of the system [46,49]. In this work, two equivalent electrical circuit models were used, which are presented in Figure 4. Table 3 presents the electrical parameter values found by fitting the equivalent electrical circuit from the experimental EIS data, obtained in a LiBr solution. In these circuits, Rs, Rp and Rinh represent the electrolyte resistance, polarization resistance and resistance at the interface of solution and inhibitor, respectively. According to figure 3, C$_{dl}$ represents double layer capacitance and C$_{inh}$ represents a capacitance at the interface of solution and inhibitor [50,51].

![Figure 2. Potentiodynamic polarization curves of type 316L SS obtained in LiBr solution with various Na$_2$MoO$_4$ concentrations at 60°C.](image)

![Figure 3. Equivalent circuit for 316L SS samples in LiBr solution, a) absence and b) presence of inhibitor](image)
Figure 4. Nyquist and Bode diagrams of type 316L SS obtained in LiBr solution with various sodium molybdate concentrations at 60°C

Slika 4. Nyquist i Bode dijagrami za čelik316L SS dobijeni u rastvoru LiBr sa različitim koncentracijama natrium molibdata na 60°C
Table 3. EIS parameters for the corrosion of 316L SS in MiBr solution containing different concentrations of Na$_2$MoO$_4$ at 60°C

Tabela 3. Parametri EIS za koroziju 316L SS u MiBr rastvoru koji sadrže različite koncentracije Na$_2$MoO$_4$ na 60°C

<table>
<thead>
<tr>
<th>Inhibitor Concentration (ppm)</th>
<th>$R_p$ (Ω)</th>
<th>$C_{dh}$ (F)</th>
<th>$R_{inh}$ (Ω)</th>
<th>$C_{inh}$ (F)</th>
<th>$R_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.155</td>
<td>-</td>
<td>-</td>
<td>2.79×10^-4</td>
<td>21000</td>
</tr>
<tr>
<td>50</td>
<td>2.54</td>
<td>6.68×10^-6</td>
<td>111</td>
<td>1.80×10^-5</td>
<td>29800</td>
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<tr>
<td>100</td>
<td>8.218</td>
<td>4.23×10^-5</td>
<td>230</td>
<td>8.42×10^-6</td>
<td>37322</td>
</tr>
<tr>
<td>200</td>
<td>10.04</td>
<td>1.67×10^-5</td>
<td>370</td>
<td>3.15×10^-7</td>
<td>138000</td>
</tr>
</tbody>
</table>

3.2. SEM investigations

Figure 5 shows the SEM micrographs of 316L stainless steel surface after electrochemical tests in lithium bromide solution containing different concentrations of Na$_2$MoO$_4$ at 60°C. In the presence of inhibitor, as expected, the number of pits is decreased in comparison to pure LiBr solution.

Figure 5. The morphology of pits generated on the surface of 316L SS after the electrochemical test in a) Libr, b) LiBr + 50ppm Na$_2$MoO$_4$, c) LiBr + 100ppm Na$_2$MoO$_4$, d) LiBr + 200ppm Na$_2$MoO$_4$

Slika 5. Morfologija jama nastalih na površini 316L SS posle elektrohemijskog testa u a) Libr, b) LiBr + 50ppm Na$_2$MoO$_4$, c) LiBr + 100ppm Na$_2$MoO$_4$, d) LiBr + 200ppm Na$_2$MoO$_4$
4. CONCLUSION

The corrosion behavior of 316L stainless steel in 850gr/l Lithium bromide in the absence and presence of 50ppm, 100ppm and 200ppm sodium molybdate was studied in this paper. The results could be summarized as below:

1. Potentiodynamic tests revealed that the addition of sodium molybdate to Lithium bromide solution, increases the corrosion resistance of 316L SS. Corrosion resistance increases with the inhibitor concentration.

2. According to the potentiodynamic polarization tests, sodium molybdate was diagnosed as mixed-type inhibitors.

3. Potentiostatic tests revealed that the frequency of pit formation on the surface of 316L stainless steel is decreased in the presence of inhibitor. This result was confirmed by scanning electron microscopy.

4. Impedance test results shows that sodium molybdate is an absorption inhibitor reducing the corrosion rate with its effect on the anodic and cathodic sites simultaneously, the corrosion rate is reduced.

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5. REFERENCES


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IZVOD

ISPVITANJE EFEKATA Na2MoO4 KAO INHIBITORA NA ELEKTROHEMIJSKO KOROZIONO PONAŠANJE NERĐAJUĆEG ČELIKA 316L U RASTVORU LiBr

Uticaj natrijum-molibdata (Na2MoO4) kao inhibitora pri njegovim različitim koncentracijama 50, 100 i 200 ppm na elektroхиemijsko korozionsko ponašanje nerđajućeg čelika 316L u LiBr rastvoru na 60°C ispitani su polarizacionim krivinama, metodama elektroхиemijske impedanske spektroskopije (EIS) i elektronske mikroskopije. Otpornost na koroziju uzorka nerđajućeg čelika 316L povećava se sa koncentracijom inhibitora do 200ppm. Povećanjem koncentracije inhibitora od 50ppm do 200ppm smanjuje se gustina korozivne struje. Ovi rezultati su potvrđeni daljom analizom koristеći skenirajući elektronski mikroskop.

Ključне rečи: natrijum molibdat, korozija, nerđajući čelik 316L, litijum bromid.

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