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Corrosion and inhibition of Cu-Zn alloys in NaCl solution by using permanganate and phosphate anions

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The effect of permanganate and phosphate anions on the corrosion of Cu-Zn alloys in NaCl solution has been studied using open circuit potential, potentiodynamic, and electrochemical impedance spectroscopy (EIS) techniques. The addition of increasing concentrations of permanganate and phosphate anions decreases the corrosion rate, which indicating the corrosion inhibition effect. The adsorption characteristics of these anions on the Cu-Zn alloy surface play a significant role in the inhibition processes. The effect of different anions on the corrosion behavior of Cu-Zn samples I and II (with different composition) was also studied in NaCl solution.

Keywords: Cu-Zn alloy, corrosion, NaCl, inhibition

1. INTRODUCTION

Alloying of Cu with other elements (e.g. Zn, Al, etc.) leads to alloys with improved mechanical properties and higher corrosion resistance. Such alloys are used extensively for condenser tubes and tube sheets in heat exchangers in power plants, oil refineries and chemical plants where resistance to corrosion by water is a consideration. Leaded metal and naval brass tube sheets are used commonly in heat exchangers cooled with seawater [1]. The electrochemical behavior of Cu-Zn alloys (brass) has been studied extensively over a wide range of experimental conditions in relation to passivation and pitting corrosion [2-4]. In neutral and alkaline solutions the passivation of brass involves the electroformation of a complex $ZnO.xH_2O$ and Cu_2O layer, as concluded from electrochemical, XPS and Auger spectroscopy data [5]. In general, passivity breakdown depends strongly on the composition of the alloy, the aggressive environment and temperature. In chloride solutions, the first step of the anodic dissolution of Cu is the formation of complex $CuCl_2^-$. In addition, it was found that during anodic polarization, there is always equilibrium between a thin layer of CuCl and a dense layer of dissolved $CuCl_2^-$ [6]. The present work aims to: 1) Characterize the effect of permanganate and phosphate anions as corrosion inhibitors of Cu-Zn alloy in NaCl solution using electrochemical methods and EIS techniques. 2) Establish the role of these anions improving the passive film resistance to the corrosion caused by chloride ions in neutral medium.

2. EXPERIMENTAL PART

Experiments were carried out in NaCl solution in absence and presence of different concentrations of potassium permanganate and sodium phosphate. All solutions were prepared from double distilled water. A. R. chemicals and new polished electrodes were used for each run. All experiments were carried out at room temperature (25° C). All solutions were used under purified nitrogen gas. Two Cu-Zn samples were used in the present work as working electrodes. The composition (wt %) of sample (I) is 78% Cu, 20% Zn and 2% Al. The composition of the second sample (II) is 69% Cu and 31% Zn. The ingots were machined in the form of short rods, each 20 mm in length and 5 mm in diameter. Each working electrode was constructed and treated following the procedure described previously [7]. A Pt sheet was used as a counter electrode. The potential was measured against Ag/AgCl electrode. The polarization measurements were run on a computerized potentiostat (Radiometer model VoltaLab 40) and VoltaMaster 4 software.

3. RESULTS AND DISCUSSION

The open circuit potentials of the two Cu-Zn samples immersed in NaCl solutions in the different concentrations were followed as a function of time, till the steady state values were attained. The steady state potential $E_{s.s}$ values approached from more negative values with increasing NaCl concentration indicating the destruction of pre-immersion passive film found on the Cu-Zn surfaces. Fig. 1 illustrates the straight line relationship between $E_{s.s}$ and NaCl concentration which satisfies the following equation:

$$E_{s.s} = a - b \text{ Log } [\text{NaCl}]$$

Symbols a and b are constants dependent upon the composition of the Cu-Zn alloy. The negative shift in $E_{s.s}$ indicates that NaCl accelerates the anodic (metal dissolution) reaction. This could be attributed to direct participation of adsorbed Cl^- ions on ionization of the alloy. Therefore, one can conclude that in NaCl solution, the corrosion of Cu-Zn is determined by polarization of the anodic controlling reaction, i.e., the corrosion process is anodically controlled. The data in Fig. 1 show that the steady state potentials of sample II are more negative than those of sample I. These results indicate that sample II suffers more corrosion than sample I. This observation may be attributed to the relatively high resistance of the sample I due to the presence of Al. The potentiodynamic polarization curves for samples (I, II) in different concentrations of NaCl solution was measured. Figure 2 indicates that an increase in NaCl concentration increases the corrosion rate for the two samples. The adsorbed Cl^- ions

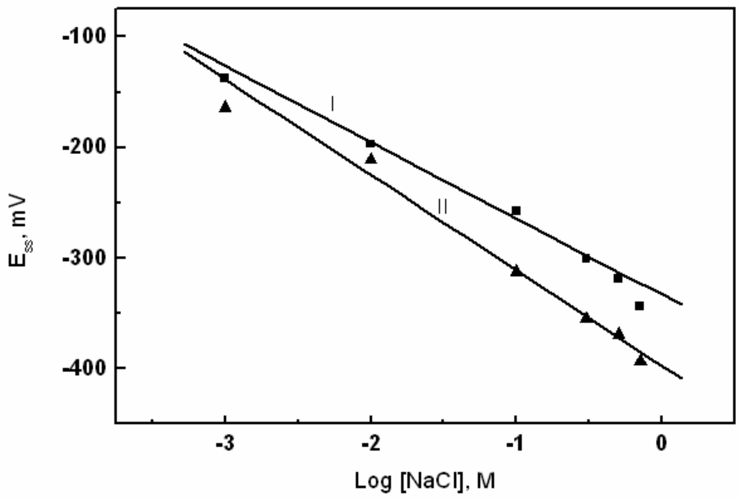

Figure 1. Variation of steady state potential ($E_{s.s}$) for samples (I, II) with the concentration of NaCl

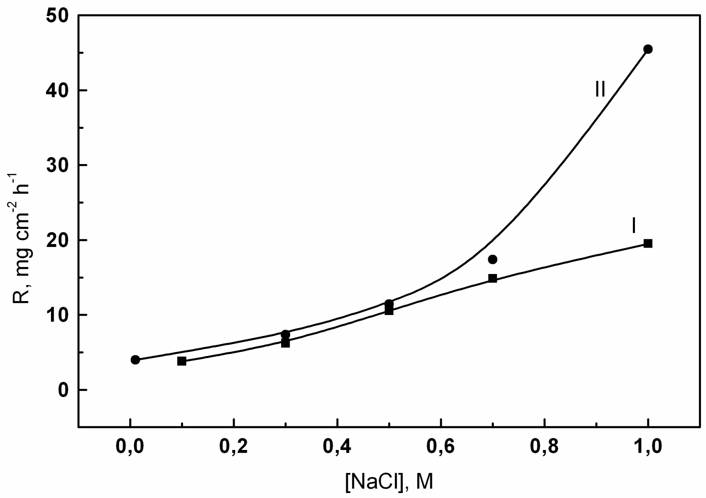

Figure 2. Corrosion rate as a function of NaCl concentrations for samples (I, II).

participate directly in the ionization of the metal atoms. The corrosion resistance of the alloy samples increase in the order: I > II, this sequence can be argued to the presence of Al in sample I. According to Pourbaix diagram for Al [8], a stable Al_2O_3 passive film formed in neutral medium (pH=4-8) and in the potential range (-1.8 to 1.1 V).

Figure 3 manifests the variation of $E_{s.s}$ of the two Cu-Zn alloy samples in 0.5 M NaCl solution containing different concentrations of MnO_4^-. It is worthy to note that $E_{s.s}$ shift to more positive with increasing the concentration of MnO_4^- in the electrolyte, according to the following equation:

$$E_{s.s} = A + B \text{ Log } [MnO_4^-]$$

Symbols A and B are constants depend on the composition of the alloy. Such behavior could be related to an increase in the anodic polarization which reflects in an increase in the inhibition efficiency of

MnO_4^- with increasing its concentration. Therefore, one concludes that the corrosion of alloys in the presence of MnO_4^- is under anodic control.

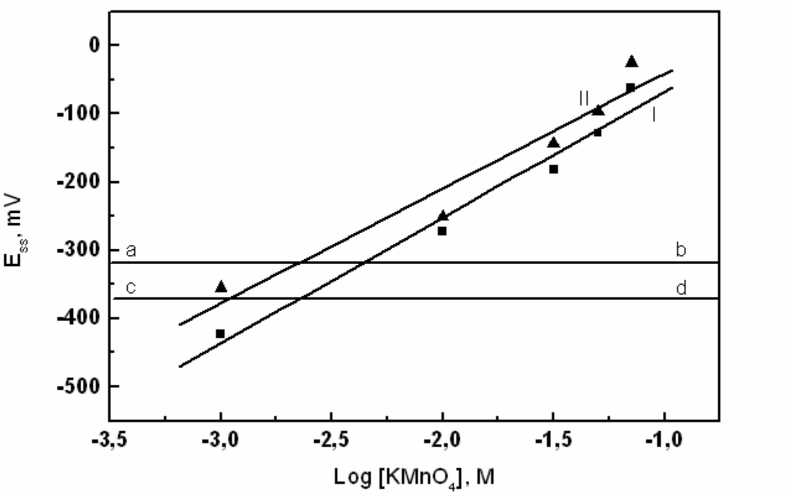

Figure 3. Variation of steady state potential ($E_{s.s}$) for samples (I, II) in 0.5 M NaCl with the concentration of $KMnO_4$. $E_{s.s}$ of sample I in 0.5 M NaCl is denoted in a-b line and $E_{s.s}$ of sample II in 0.5 M NaCl is denoted in c-d line.

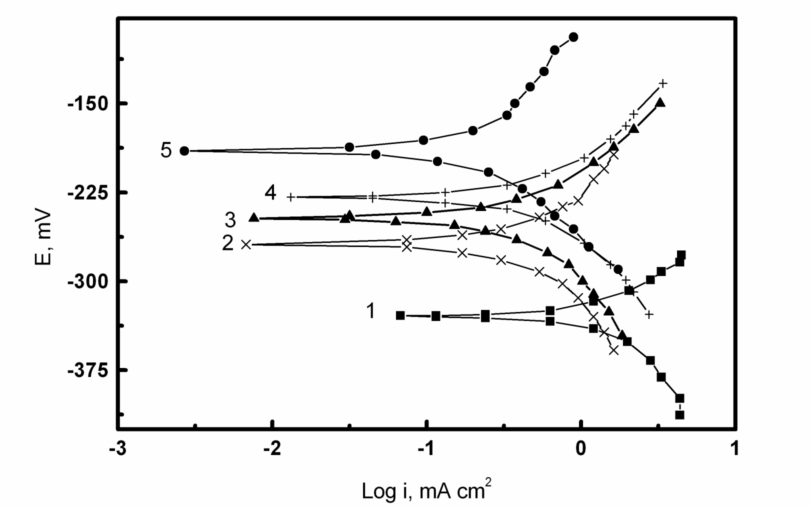

Figure 4. Polarization curves for sample I in 0.5 M NaCl solution in the presence of different concentrations of $KMnO_4$: 1) 0.0, 2)0.01, 3)0.03, 4)0.05, and 5)0.1 M.

The effect of adding increasing amounts of permanganate and phosphate anions to 0.5 M NaCl on the potentiodynamic polarization curves was investigated (Fig. 4, as example). Figure 5 indicates that the increasing of MnO_4^- and PO_4^{3-}concentrations leads to decreasing the corrosion rate. This result is suggesting that these anions are acting as corrosion inhibitors for the two alloys in NaCl solutions. The calculated inhibition efficiency (IE) from the corrosion rate can be indicated in Fig. 6. The inhibition efficiency of MnO_4^- or PO_4^{3-} ions increases with increasing of their concentrations. The inhibiting effect of these anions can be explained on the basis of the competitive adsorption between these anions and the aggressive Cl^- ions on the passive electrode surface and thus retards their

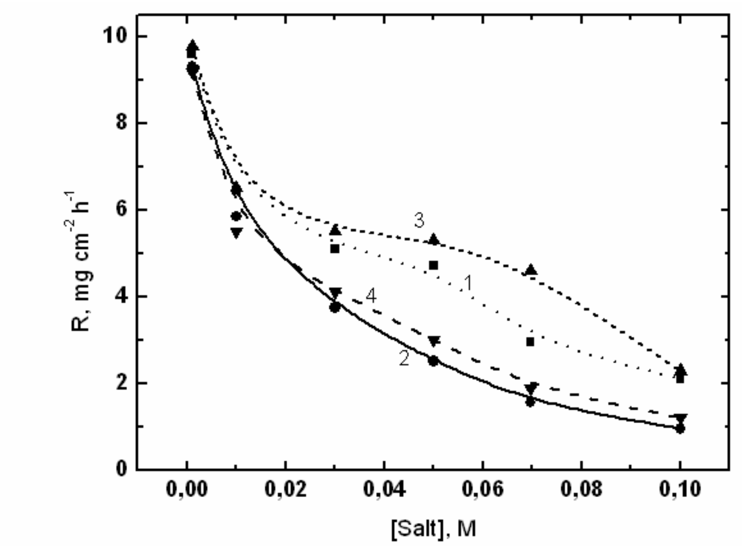

Figure 5. Corrosion rate for different samples in 0.5 M NaCl as a function of inhibitor concentrations: 1) sample I in $KMnO_4$, 2) sample II in $KMnO_4$, 3) sample I in Na_3PO_4 and 4) sample II in Na_3PO_4.

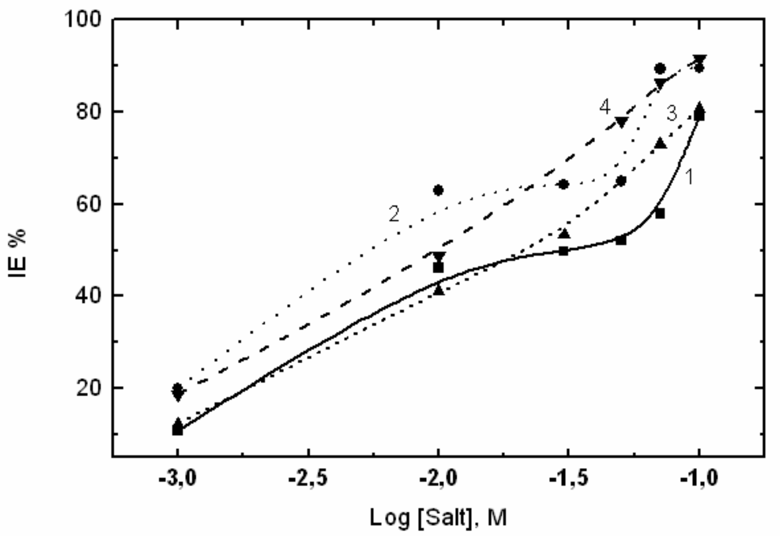

Figure 6. Inhibition efficiency for different samples in 0.5 M NaCl as a function of inhibitor concentrations: 1) sample I in $KMnO_4$, 2) sample II in $KMnO_4$, 3) sample I in Na_3PO_4 and 4) sample II in Na_3PO_4.

corresponding destructive action [9]. The inhibitive anions may be incorporated into the passive layer on the alloy surface, forming an improved stability against the aggressive ions. The increase of the Mn content (from inhibitor) in the passive layer leads to a significant increase in corrosion resistance [10, 11]. The protective properties of phosphate anion is directly dependent on the pH of the solution, an increase in the concentration of Na_3PO_4 is accompanied by an increase in the pH (at 0.1 M Na_3PO_4 is 6.05) and consequently an increase in the stability of the passive film obtained.

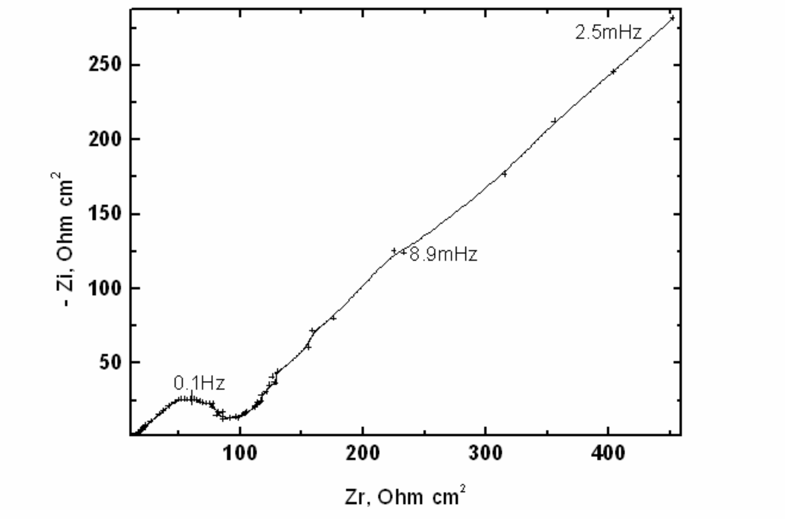

Figure 7. Nyquist plot for sample I in 0.1 M NaCl.

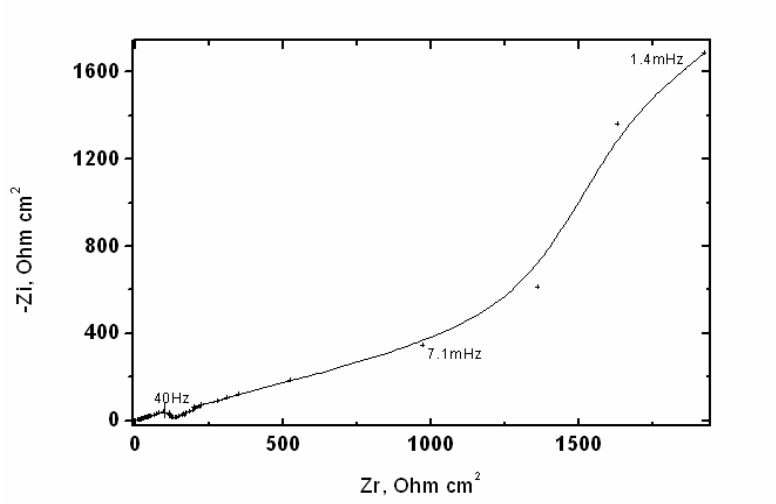

Figure 8a. Nyquist plot for sample I in 0.1 M NaCl and 0.1 M $KMnO_4$.

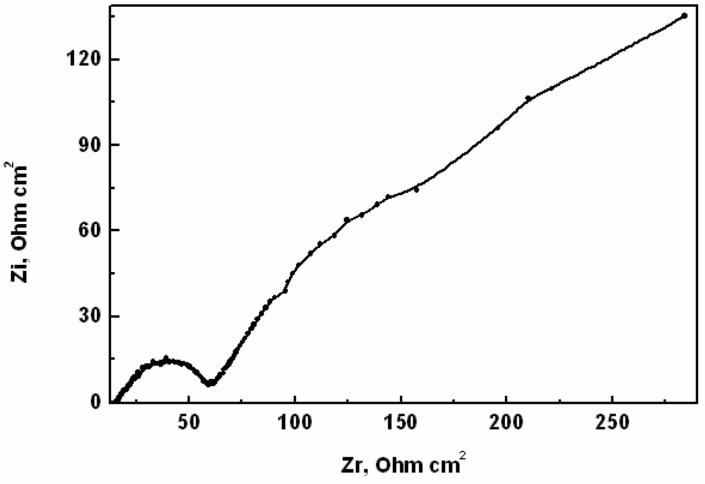

Figure 8b. Nyquist plot for sample I in 0.1 M NaCl and 0.1 M Na_3PO_4.

Figure 7 shows the impedance complex diagrams (Nyquist plot) of sample I in 0.1 M NaCl. The impedance diagram gave a semicircle type appearance, indicating that the corrosion of alloys is mainly controlled by charge transfer process. The impedance measurements were carried out at the open circuit potential, i.e. at the corrosion potential (E_{corr}). The impedance complex diagrams of samples (I, II) in 0.1 M NaCl in presence of each MnO_4^- and PO_4^{3-} was shown in Figure 8 (as example). The impedance diagrams in Figs. 7 and 8 show that the charge transfer resistance of different alloys in 0.1 M NaCl increases in the presence of MnO_4^- or PO_4^{3-}. Electrochemical theory shows that the reciprocal of the charge transfer resistance is proportional to the corrosion rate [12]. The corrosion rate of Cu-Zn alloys in 0.1 M NaCl is higher than that in presence of MnO_4^- or PO_4^{3-}. The corrosion rate in 0.1 M NaCl in the presence of 0.01 M MnO_4^- is lower than that in the presence of the same concentration of PO_4^{3-}. This indicates that PO_4^{3-} is more efficient than MnO_4^- in the inhibition of the Cu-Zn alloys; this is in good agreement with the d.c. polarization results.

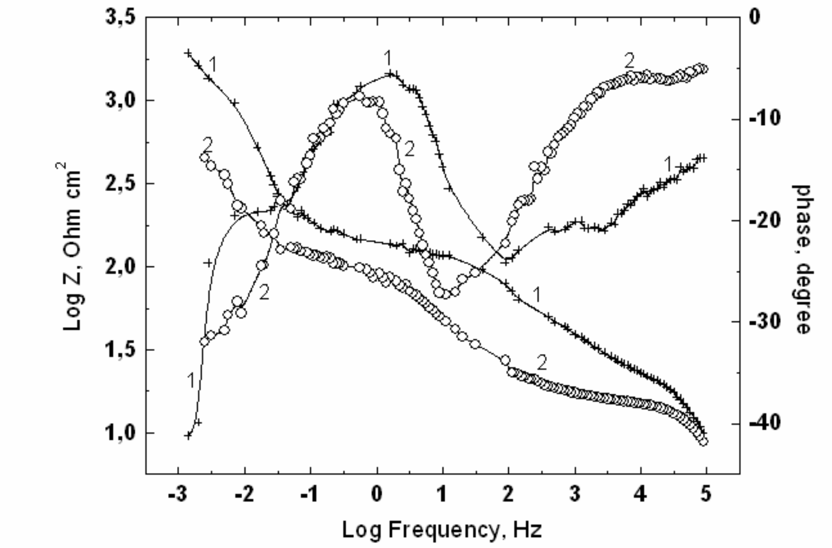

Figure 9a. Bode plot for: 1) sample I in 0.1 M NaCl and 2) sample I in 0.1 M NaCl and 0.1 M $KMnO_4$

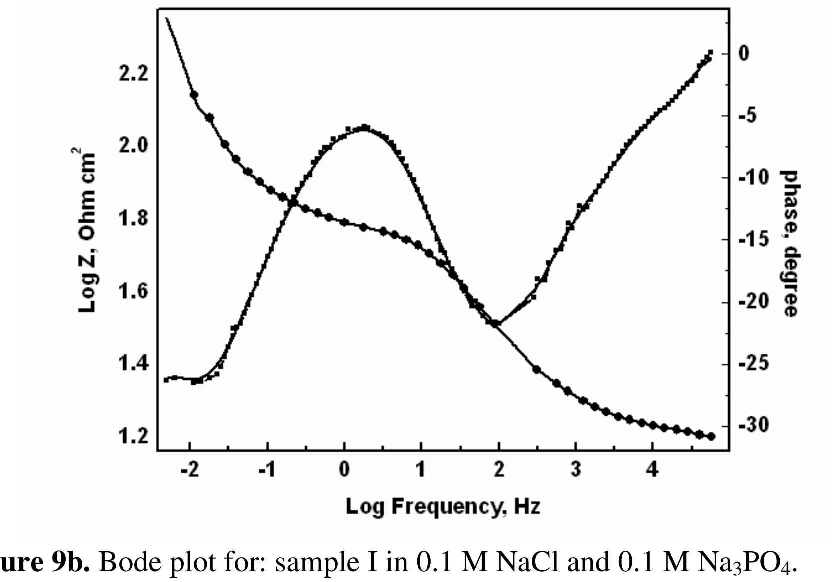

Figure 9b. Bode plot for: sample I in 0.1 M NaCl and 0.1 M Na_3PO_4.

In the ω versus θ Bode plots, there is one phase maximum (Fig. 9, as example), i.e. one relaxation process. This result indicates that there are one charge transfer processes taking place at the alloy-electrolyte interface. This process is due to the diffusion of different component (Cl^-, MnO_4^- or PO_4^{3-} ions) at the alloy-electrode interface. The Bode plot (ω versus |Z|) shows the presence of inhibitor leads to decreasing of impedance values, which may be due to the adsorption of different corrosion products and inhibitor species (MnO_4^- or PO_4^{3-}) on Cu-Zn alloy surface. The comparison of impedance in Bode plot for samples I or II (Fig. 9, as example) indicates that it is increase in the order: I > II, this sequence can be argued to the presence of Al in sample I as discussed above.

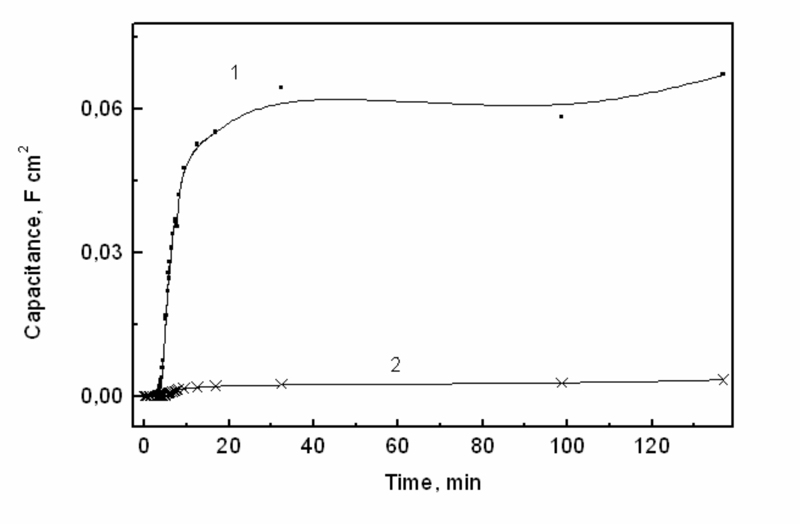

Figure 10. Dependence of the capacitance on the time: 1) sample I in 0.5 M NaCl, 2) sample I in 0.1 M NaCl and 0.1 M $KMnO_4$

Figure 10 shows the dependence of the capacitance of the alloy solution interface in the absence and presence of MnO_4^- on the time. It appears that the capacitance of alloy/solution interface is lower than that in NaCl without inhibitors. This behavior is mainly due to the adsorption of the inhibitor molecules at the alloy solution interface. The curves in the figure show that the presence of MnO_4^- causes a decrease in the capacitance of the alloy solution interface, which is probably due to the strong adsorption of the molecules of these substances at the interface.

4. CONCLUSIONS

The permanganate and phosphate anions act as inhibitors for the corrosion of the two alloy samples (I, II) in 0.1 M NaCl. The inhibition efficiency increases with the increasing of the concentration of permanganate or phosphate anions. The presence of these anions inhibits the corrosion of alloy samples in 0.5 M NaCl solutions in the order: phosphate > permanganate. The inhibition is due to the adsorption of the inhibitor anions on the sample surface.

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