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Investigation of Effect of ClO_4^- Ions on the Growth of Indium Oxide Films on In Electrode in Dilute $Na_2B_4O_7$ Solution by Potentiometric Technique

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Oxide film growth and formation on In were investigated in 0.01 M $Na_2B_4O_7$ solutions under natural corrosion conditions by a potentiometric technique. The addition of $NaClO_4$ to the 0.01 M $Na_2B_4O_7$ solution reduces the rate of oxide film growth. The steady-state potential, E_{st}, was found to depend on the added amount of ClO_4^- ions and shifts to a more active direction, following the equation, $E_{st} = \alpha - \beta \log C_{NaClO4}$. The rate of oxide film formation was found to follow a direct logarithmic relation. The appearance of two segments on E-log t plots confirms the formation of inner and outer oxide layers on the indium surface. The increase in the solution temperature reduces the rate of oxide film repair and shifts E_{st} to more negative values. The rate of oxide film repair is lowered by increasing the added amount of $NaClO_4$. Some micrographs investigated under SEM indicated the absence of any signs of corrosion indication in the free $Na_2B_4O_7$ solution with the presence of some scratches in the case of ClO_4^- anions. The activation energies of the oxide film growth were computed in 0.01 M $Na_2B_4O_7$ solution in the absence and presence of $NaClO_4$ and were found to vary between 7.45 and 28.89 KJ/mol which is less than 40 KJ/mol that confirms that the rate of oxide film formation is controlled by a diffusion process.

Keywords: Indium, $NaClO_4$, Oxide film formation, Oxide film repair, Potentiometry.

1. INTRODUCTION

In and In oxides are beneficial for many electronic purposes, diaphanous conducting material, as well as in electrocatalytic activities [1]. The electrochemical investigations of indium and its alloys are carefully attributed to its merchant implementation in optoelectronics and alkaline batteries [2]. Most of the awareness has been centralized on the investigation connected to the formation of indium oxides, due to the great prominence in the industry fields. Pellucid immediate metal oxide films with major In_2O_3 and Sn-doped In_2O_3 have been frequently utilized in an assortment of implementations such as liquid crystal displays, solid-state sensors, solar cells, and cathode ray tubes [3-5]. The extreme collective procedures of In_2O_3 and Sn-doped In_2O_3 film formations are the reactive deposition methods [6-14], thermal sedimentation [15-17], and solution growth [18–21]. The optoelectronic and structural characteristics of In_2O_3 films have also been excessively examined [1–21]. The prospect of utilizing In-oxide as a sensitive electrode for O_2 in some electronic types of equipment with a solid oxide media was investigated by Kuzin et al. [22]. The implementation of In-oxide as an electrode suitable for investigating the mechanism in the bioelectrochemical reactions has also been examined utilizing different techniques [23- 25].

The thin oxide films formed on In in borax electrolytes are examined by open circuit potential, galvanostatic [26,27], cyclic voltammograms, and electrochemical impedance spectroscopy measurements [28]. The attitude of In pending the anodic oxidation sympathizes on many sides with the anodization of valve metals and as a suitable catalyst for the electrooxidation reactions [29]. The kinetics and reactivity of the utilized oxide films were investigated early as a function of the potential domain, time-diffusing process, and electrolyte concentration [30,31].

Whatever the kind of the formed oxide film on the active metals in many aqueous media the existence of some of the aggressive ions like chlorides, chlorate, and perchlorate can reduce the rate of oxide film formation and initiate the pitting corrosion on some of the active electrodes in different electrolytes [32-47].

This study aims to examine the role of $NaClO_4$ on the oxide film formation on an indium metal in 0.01 M $Na_2B_4O_7$ electrolyte utilizing potentiometric measurements. SEM is utilized to examine the surface of some examined indium metal samples after inundation in 0.01 M $Na_2B_4O_7$ without and with 0.05 M $NaClO_4$, at 25 °C. The effect of temperature on the oxide film formation on In in 0.01M $Na_2B_4O_7$ solution without and with 0.005 M $NaClO_4$ was examined and discussed.

2. EXPERIMENTAL

The purity of indium metal was 99.99% in a form of a cylindrical rod with a diameter of 0.80 cm thick (Aldrich). This rod was introduced into a Pyrex glass tube using an Araldite substance with a free metal contact area of 0.503 cm^2. A suitable Cu wire was used for electrical connection by soldering to the end of the indium rod, not in contact with the test electrolyte. The change in potential of the indium metal was followed using a saturated calomel electrode as a reference electrode, SCE. Before each run, the indium electrode was polished thoroughly using a series of various grades of very fine polished papers. After that, the electrode was washed with distilled water, and rinsed with a mixture of ethanol-acetone, followed by doubly distilled water before inundation in the examined electrolyte.

The change in the In electrode potential was pursued with immersion time till reaches the steady state potential, E_{st} for a period extended to 5 h utilizing a Wenking potentiometer type PPT70. For each run, duplicate measurements were done and the average potential value was taken. The squander in In electrode potential values was predestined as ≤ ± 0.003 V. The E_{st} value was manifested as that value that did not alter by more than ± 0.001 V/10 min.

The investigated electrolytes were attained from AR chemicals and bidistilled water. The $Na_2B_4O_7$ and $NaClO_4$ electrolytes were prepared by dissolving the required amounts of these salts in suitable volumes of distilled water. The used electrolytic cell has a double wall jacket through which water, at the adjusted temperature, was circulated. Experiments were done at a constant temperature, 25 ± 0.1°C, except those carried out with the influence of temperature. The cell temperature was adjusted by utilizing an electronic thermostat, Poly Science (USA).

Scanning electron microscopy, SEM was utilized to investigate some In species, after inundation in the investigated electrolytes for a period of 5 h, utilizing a Jeol scanning electron microscope, JSM-T 100 (Japan).

3. RESULTS AND DISCUSSION

3.1. Effect of $NaClO_4$ concentration

The data in Fig 1 depicts the potential time plots of the In metal immersed in 0.01 M $Na_2B_4O_7$ electrolytes (naturally aerated) free of and mixed with various amounts of $NaClO_4$ solutions. As can be seen from these curves, in the free sodium borate electrolyte, the potential starts at a more negative initial value (-734 mV_{SCE}) and shifts to less negative values to reach a steady potential (E_{st} = - 479 mV_{SCE}), after a period of ~280 min. The shift of the indium metal potential towards less active values, when inundated in a naturally aerated $Na_2B_4O_7$ solution, indicates that the pre-immersion oxide film held by the metal surface is not sufficient to realize passive oxide film on the metal surface [47]. The healing and thickening of the In oxide films is still continual until passivity is achieved. This finding can be explained based on the uninterrupted growth of the indium oxide layer on the investigated metal surface [48].

However, the same behavior is noticed when $NaClO_4$ is included in the aerated $Na_2B_4O_7$ solution. The E_{st} value is attained from negative potentials and takes more active values with increasing the added amount of $NaClO_4$. Such attitude suggests the continuous repair of the oxide film on the indium electrode to an extent that is reduced by raising the added amount of the ClO^-_4 ions. In the studied range of the added amount of $NaClO_4$, the oxide film repair by $Na_2B_4O_7$ commands that of film annihilation by the corrosive ClO_4^- ions [49]. The E_{st} varies linearly with the log C, for the added $NaClO_4$, Fig 2, obeying the equation:

$$E_{st} = \alpha - \beta \log C_{NaClO4} \qquad (1)$$

where α and β are constants. The constant α resembles the E_{st} value in an electrolyte containing 1.0 M $NaClO_4$ which amounts to -760 mV and the slope β equals 80 mV/log. The same behavior was also attained for different active metals when immersed in various electrolytes [47, 50-55].

The SEM micrographs depicted in Fig 3 (A&B) illustrate the surface of the indium metal specimens next to the inundation for a period of 5 h in 0.01 M $Na_2B_4O_7$ without and with 0.05 M $NaClO_4$, successively. The micrograph of Fig 3A appears with a surface of smooth shape without any indication of the corrosion influence, while the micrograph Fig 3 B depicted some scratches with a non-homogenous surface.

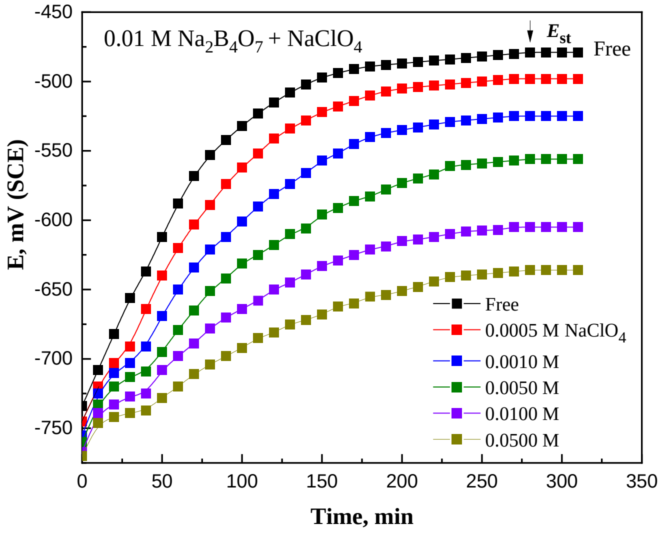

Figure 1. The *E-time* plots for In electrode in 0.01 M $Na_2B_4O_7$ free of and mixed with various amounts of $NaClO_4$ solutions, at 25 °C.

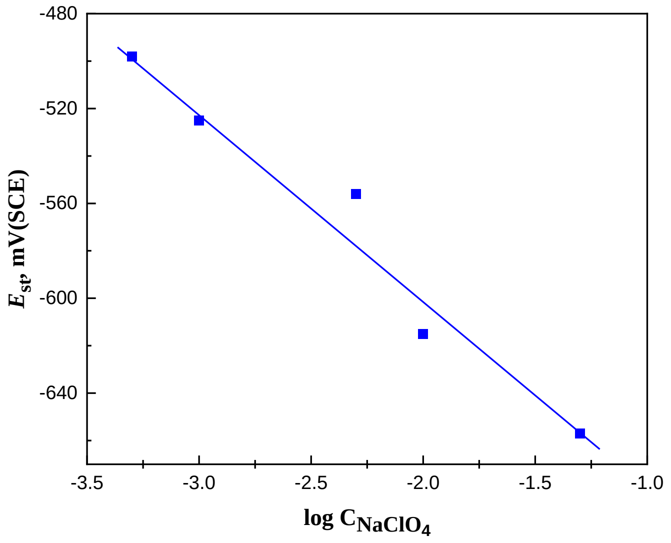

Figure 2. The E_{st} - log C_{NaClO4} plots for In in presence of 0.01 M $Na_2B_4O_7$, at 25°C.

The route by which the potential of the In metal attains the E_{st} value after an inundation period in the examined electrolytes is of solicitude. As depicted in Fig 4, the potential E changes with the log t, for all $NaClO_4$ solutions, obeying the relation [35, 47, 50-55]:

$$E = \alpha_1 + \beta_1 \log t \quad (2)$$

where α_1 and β_1 represent the equation constants. The value of β_1 represents the slope value of the constructed E- log t curves and is reduced slightly by the more added amount of $NaClO_4$. Such attitude signalizes that the oxide film repair on the indium metal surface, under the examined conditions obeys a direct logarithmic relation. The plots of Fig 4 are constructed from two different segments followed by E_{st}. Such attitude can be explained as due to the growth of a barrier indium oxide film adjacent to the metallic surface and an outer porous one exposed to contact with the examined electrolytes. This finding is similar to that found on the Al surface when examined in acidic solutions under natural corrosion conditions [35].

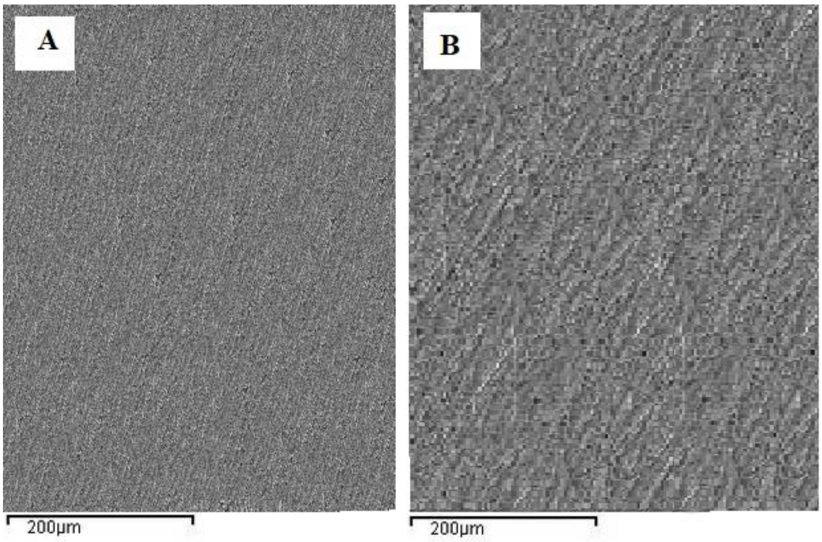

Figure 3. SEM micrographs of the In specimens after inundation for a period of 5 h in 0.01 M $Na_2B_4O_7$ without (A) and with 0.05 M $NaClO_4$ (B), respectively.

Scientists have suggested various models explaining the linear relationship between the In potential, E, and the log t. According to one of such models, the growth of the indium oxide layers is dominated by the ions and electrons diffusion under the impact of a concentration gradient and an electric potential [52–57]. Cabrera and Mott examined the kinetics of growing oxide film on some metals, at low temperatures [58], where cation migration can take place by the effect of a potential build-up across the growing oxide layer [59]. Shimizu et al. [60] discussed the linear relationship between the potential-time curves based on electron tunneling via the oxide film growth. Burstein and Organ [61, 62], suggested that oxide film growth obeys a high field relation [63]. Chao and Sato assumed the direct logarithmic behavior to explain the kinetic relation for the rise in the examined electrode potential versus the log t of immersed period [64, 65].

As mentioned previously [48] the change of the potential of the investigated metal, *E*, with the inundation period, *t*, can be represented by the relation:

$$E = \text{const.} + \frac{2.303\delta^-}{\beta}\log t \tag{3}$$

where δ^- expresses the rate of oxide film growth, and β refers to a constant expressed by the equation [47, 48]:

$$\beta = \left(\frac{n\,\mathrm{F}}{\mathrm{RT}}\right)\alpha\delta' \tag{4}$$

where α refers to the transfer coefficient analogous to that faced in normal electrochemical reactions [66], ($0 < \alpha < 1$). In addition, δ' is the width of the energy barrier surmounted by the ion during transfer. Supposing that the thinking of the oxide film on In electrode is controlled by the diffusion of the In^{3+} ions out of the oxide/metal interface. The constant β is computed in the case of In to be 58.5 nm/V.

From the slope values of the gained segments, the *E*-log *t* relation, depicted in Fig 4, the rate of oxide growth, δ^-_1 and δ^-_2, in 0.01 M $Na_2B_4O_7$ solutions free of and mixed with different amounts of $NaClO_4$, at 25°C, could be computed, Table 1. Fig 5 depicted the variation of the rates of oxide thickening, δ^-_1, and δ^-_2, against the logarithmic concentration of $NaClO_4$. Straight lines are gained with slopes of 0.3 and 0.5 nm/ unit decade, for the first and second segments, successively. Along the lower parts, the rate of potential build-up is found to increase gradually and depends on the concentration of the added $NaClO_4$.

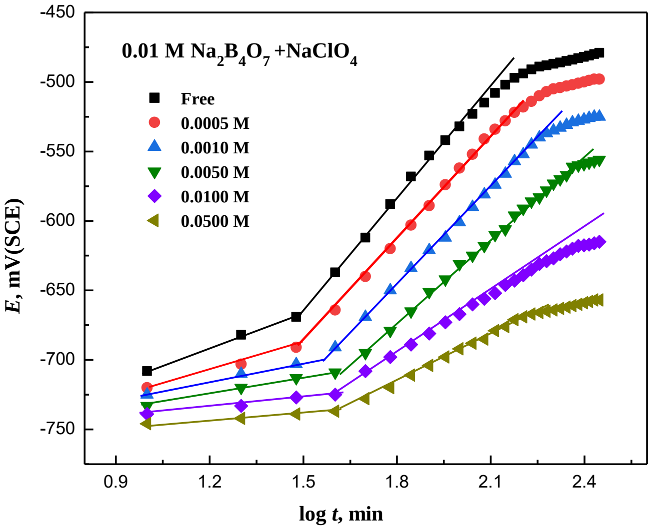

Figure 4. The *E*- log *t* curves for In in 0.01 M $Na_2B_4O_7$ without and with $NaClO_4$.

Examination of the plots of Fig 4, manifests that the initial rates of oxide film growth of the first and second layers on indium metal in 0.01 M $Na_2B_4O_7$ solutions are reduced with more added amounts of the $NaClO_4$ electrolyte. Fig 5 depicts the inverse linear relationships for the double logarithmic plots between the rates of oxide film growth and the molar concentration of the added $NaClO_4$. A tenfold increase in the added amount of $NaClO_4$ gives rise to a reduction in the initial rate of oxide film repair by only 2.5 and 1.2 for the first and second layers, successively.

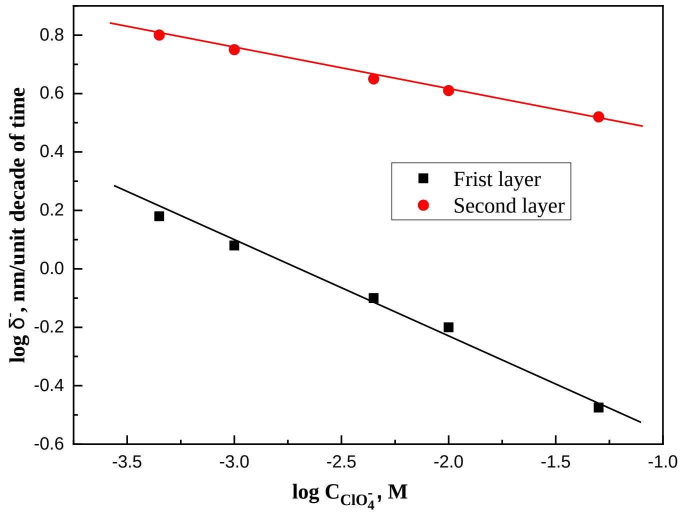

Figure 5. The log $(\delta^{-}_{1})_2$ – log C_{ClO4^-} relation for In in 0.01 M $Na_2B_4O_7$, at 25 °C.

Table 1. The values of δ^{-}_{1}, and δ^{-}_{2}, on the In electrode at different additions of the $NaClO_4$ in 0.01 M $Na_2B_4O_7$, at 25 °C.

0.01 M $Na_2B_4O_7$ + *x* M $NaClO_4$	δ^{-}_{1}, nm/unit decade	δ^{-}_{2}, nm/unit decade
Free	2.089	6.840
0.0005 M	1.513	6.310
0.0010 M	1.202	5.623
0.0050 M	0.794	4.467
0.0100 M	0.631	4.073
0.0500 M	0.335	3.311

When indium is inundated in an electrolyte, the formed oxide film is attributed to the lower energy of the In^{+3}– O bond, and this reaction can be represented by the following equation [67]:

$$2\,In + 3H_2O \leftrightarrow In_2O_3 + 6H^{+} + 6e^{-} \qquad (5)$$

The anodic behavior of indium in Na-borate solution was suggested to be under mixed control; the initial state of an indium oxide film formation includes a raid charging step followed by a slower diffusion one. Up to such layer, the growth of the barrier oxy-hydrate film takes place through base-catalyzed hydrolysis of the surface oxide with a transformation from a gel-like oxide structure, InOOH, into a more stable crystalline form, In_2O_3 at a more noble potential. The formed In_2O_3 has a high electric conductivity[68]. At high concentrations of Na-borate solution, there was a tourney between oxide film growth and dissolution, and/or, there was some ability to form a complex between In^{+3} and borate ions [69], if it happened, E_{st} shifted to more negative potentials.

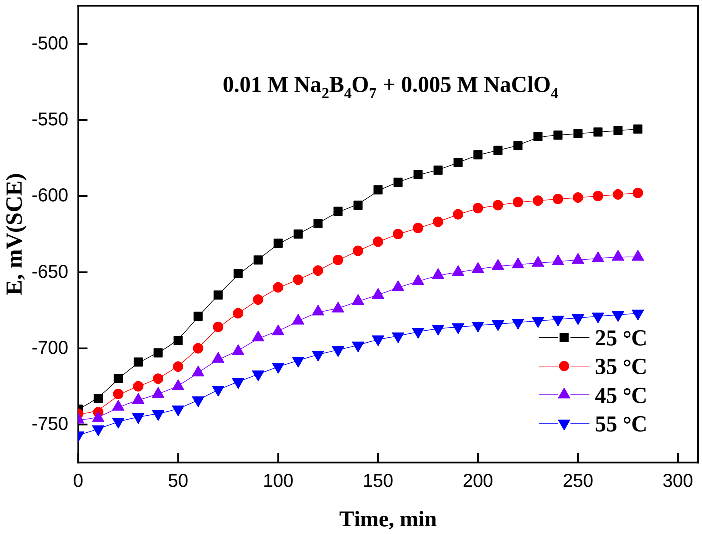

Figure 6. The *E*-*t* plots of the In electrode in 0.01 M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$, at various temperatures.

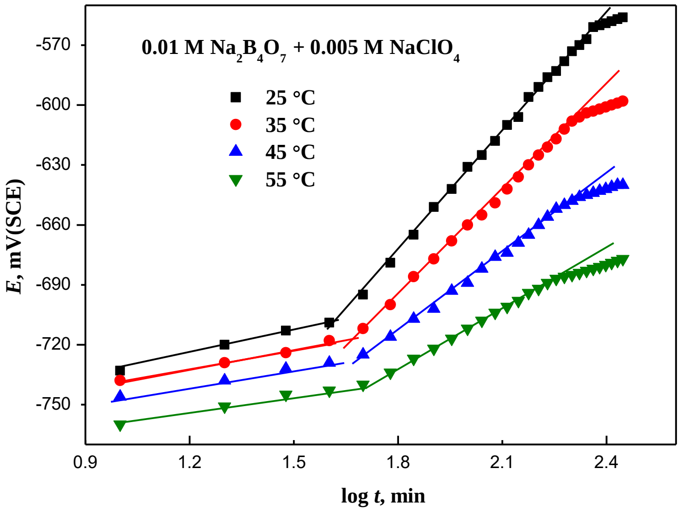

Figure 7. The *E*-*t* plots of the In electrode in 0.01M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$, at various temperatures.

3.2. influence of temperature

The effect of temperature (varying between 25 and 55 °C) on the behavior of In immersed in 0.01M $Na_2B_4O_7$ solution free-of and containing 0.005 M $NaClO_4$ solutions is carried out under natural corrosion conditions. Fig 6 depicts the potential time curves for In electrode immersed in 0.01M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$ solution, at various temperatures. Similar data are gained in 0.01M $Na_2B_4O_7$ solution free-of $NaClO_4$ (curves not shown). Fig 7 shows the *E*- log *t* curves for In electrode in 0.01M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$ solution, at various temperatures. Inspection of the data depicted in Figs 6 &7 and similar ones indicates that the increase in the temperature shifts the E_{st} into the active direction in the case of $Na_2B_4O_7$ free-of and containing 0.005 M $NaClO_4$. Also, the rise in the temperature decreases the slope of the first and second segments in Fig 7, owing to the reduction in the rate of oxide formation.

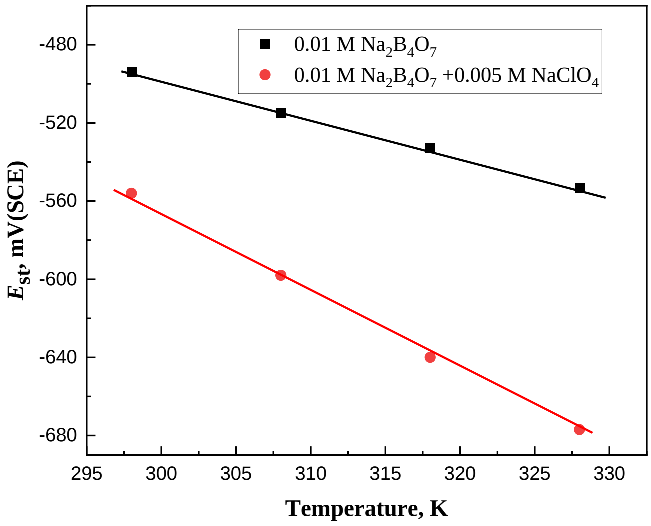

Figure 8. The E_{st} - temperature plots for In electrode in 0.01M $Na_2B_4O_7$ free-of and containing 0.005 M $NaClO_4$.

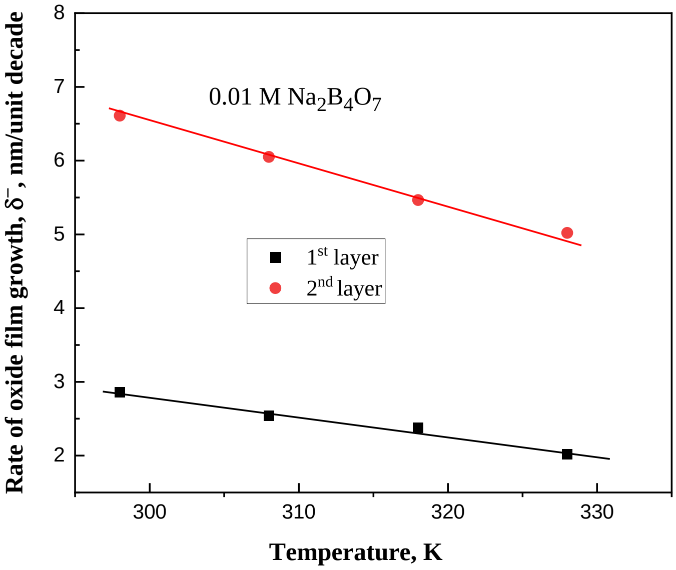

Figure 9. The variation of the rate of oxide film growth with temperature for In in 0.01 M $Na_2B_4O_7$.

The shift of the E_{st} into the negative direction with the solution temperature is depicted in Fig 8. The inverse straight-line relations confirm the destruction of the oxide film by shifting the E_{st} into the negative direction by 1.95 and 4.05 mV/ °C in the case of 0.01M $Na_2B_4O_7$ and 0.01M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$, respectively. The computed rates of oxide film formation δ^-_1 and δ^-_2 on the In electrode surface are plotted against the absolute temperatures, K, as shown in Fig 9. An inverse relation between the two variables (δ and temperature, K) confirms that as the temperature increases, the rate of oxide film repair is reduced, due to the enhancement of the destruction of the oxide film [52].

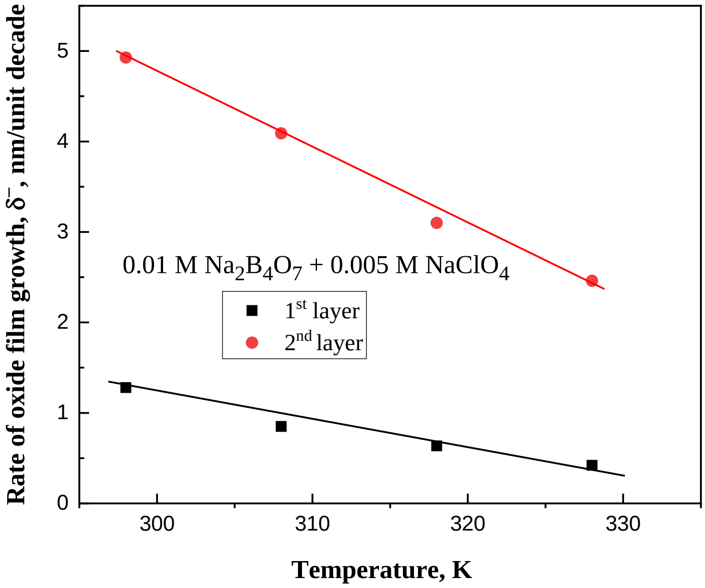

Figure 10. The variation of the rate of oxide film growth with temperature for In in 0.01 M $Na_2B_4O_7$ containing 0.005 M $NaClO_4$.

The activation energies (E_a) for oxide film repair on In in 0.01 M $Na_2B_4O_7$ free-of and mixed with 0.005 M $NaClO_4$ are computed utilizing the Arrhenius-type relation [70-72]:

$$\log \delta^- = \log A - \frac{E_a}{2.303\ RT} \tag{6}$$

where A is the Arrhenius constant, E_a is the apparent activation energy, R is the universal gas constant, pre-exponential factor, and T is the absolute temperature. The logarithm of the rate of oxide film growth for the two layers, δ^-_1 and δ^-_2 can be drawn against 1/T, Arrhenius equation, and are depicted in Figs 11 and 12. The activation free energy, E_a, of the oxide film repair on the In electrode in 0.01M $Na_2B_4O_7$ without and with 0.005 M $NaClO_4$ are computed and listed in Table 2. The low values of E_a (< 40 kJ/mole) indicate that the oxide film repair on the In metal is controlled by a diffusion process [73–76]. The computed activation free energy is higher in the presence of $NaClO_4$ could be attributed to the difficulty of the formation of oxide layers when ClO_4^- ions are added.

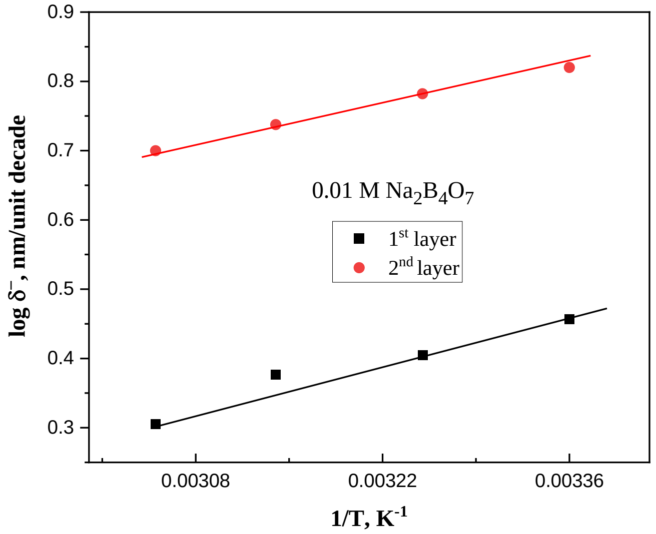

Figure 11. Arrhenius plots of oxide film growth, δ$^-$, for In immersed in 0.01 M $Na_2B_4O_7$.

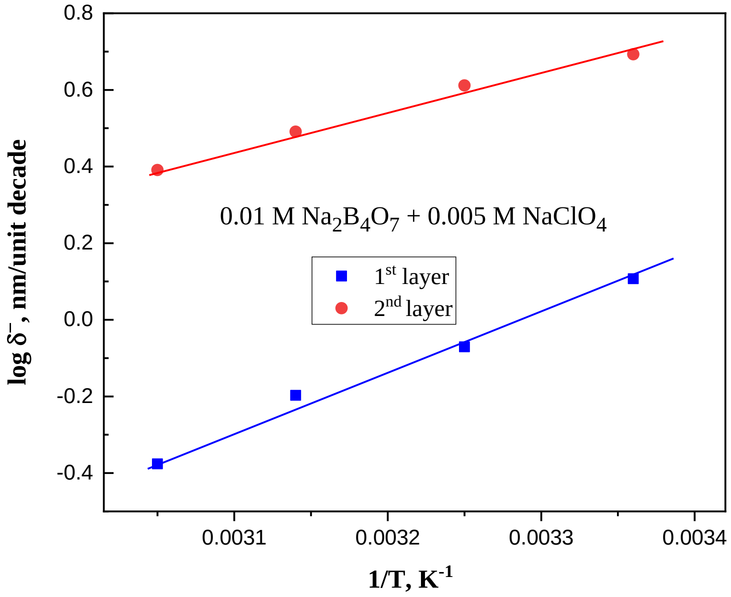

Figure 12. Arrhenius plots of oxide film growth, δ$^-$, for In immersed in 0.01 M $Na_2B_4O_7$ mixed with 0.005 M $NaClO_4$.

Table 2. The free activation energies, E_a, of the oxide film formation on In in 0.01 M $Na_2B_4O_7$ without and with 0.005 M $NaClO_4$

Solution composition	The activation energy, E_a, kJ/mol of oxide film formation on In electrode surface	
	First oxide layer	Second oxide layer
0.01 M $Na_2B_4O_7$	8.83	7.45
0.01 M $Na_2B_4O_7$ +0.005 M $NaClO_4$	28.9	18.8

4. CONCLUSION

From the potentiometric study of the corrosion of In immersed in naturally aerated 0.01 M $Na_2B_4O_7$ electrolytes devoid of and containing various amounts of $NaClO_4$, the following features could be depicted:

i- The E_{st} values are attained from negative values signalizing the oxide film repair.

ii- E_{st} depends on the ClO_4^- ions concentration, *C*, obeying the relation, $E_{st} = \alpha - \beta \log C$.

iii- The rates of oxide film repair for the inner and outer layers were found to obey a direct logarithm law.

iv- The rate of oxide film repair is reduced with more added amounts of $NaClO_4$, as well as the temperature is raised, owing to the partial destruction of the formed oxide film.

v- The free activation energies of oxide film repair are computed to be less than 40 kJ/mole, proving that the oxide film repair is controlled by a diffusion process.

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