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## Features of the local activation of aluminum in the presence of bicarbonate ions

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### Abstract

The purpose of the article is to study the effect of bicarbonate ions on the local activation of aluminum at a temperature of 25 °C.

The features of local activation of aluminum in the presence of bicarbonate ions ( $2 \cdot 10^{-4}$ – $4 \cdot 10^{-3}$  M) were studied using the methods of voltammetry, chronoamperometry, optical and scanning electron microscopy, and X-ray spectral microanalysis.

As a result, we established the range of sodium bicarbonate concentrations, in which there is local activation of aluminum; obtained experimental data on the dependence of the main quantitative characteristics of the process (potential of pitting formation, potential of local activation, and induction period) on the concentration of sodium bicarbonate. Formal kinetic approach was used to propose a mechanism for the local activation of aluminum in hydrocarbonate media.

**Keywords:** Sodium bicarbonate, Aluminum, Local activation, Passivation, Voltammetry, Chronoamperometry, Scanning electron microscopy

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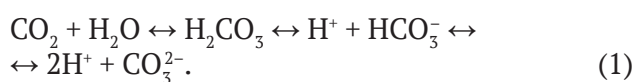


## 1. Introduction

Hydrogen carbonates mainly enter surface waters as a result of natural processes of chemical weathering and dissolution of carbonate rocks or aluminosilicates, as well as with waste water from chemical, silicate, and soda industry enterprises. Bicarbonate ions are one of the main anions present in natural water which is supplied to water and heat supply systems. The equipment of these systems can be made of various metals and alloys, including aluminum, copper, steel, etc. [1–5].

According to previous studies [6, 7], copper and iron are prone to passivation and localized damage depending on the salt content in the hydrocarbonate solution. For example, in [8, 9], it was found that passive layers formed in diluted electrolytes ( $C(\text{CNaHCO}_3) \leq 0.08 \text{ M}$ ) have low protective characteristics, and  $\text{HCO}_3^-$  ions act as pitting corrosion activators and cause metal depassivation if local activation potentials exceed the corrosion potential. With an increase in the concentration of  $\text{HCO}_3^-$  ions, the protective properties of the oxide film in relation to pitting formation (PF) increase, which is due to the stabilization of the passive film on copper and iron under the action of malachite or basic iron carbonate formed under these conditions, respectively. In contrast to the anodic behavior of copper and iron in dilute solutions, they have a wide region of passivity (up to the potential of oxygen release) in more concentrated solutions ( $C(\text{NaHCO}_3) = 0.1 \text{ M}$ ). Scanning electron microscopy (SEM) in this case does not record any pitting (PT) on the above-mentioned metals after their anodic oxidation [10].

Another approach was proposed in [11, 12]. According to it, PF on copper is not associated with the special properties of  $\text{HCO}_3^-$  ions, which have a weak activating ability, but is determined by the increasing value of pH of solutions in concentrated media, which leads to a deeper passive state of the metal. The effect of pH is also manifested in the change in the ratio of  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . Under equilibrium conditions, there is a balance between all four forms [3, 4, 13]:



At pH = 4.3, water contains practically only  $\text{CO}_2$ . With an increase in pH, the  $\text{HCO}_3^-$  content increases, at pH = 8.35 only  $\text{HCO}_3^-$  ions are present in water, and at pH ~ 12, there are only  $\text{CO}_3^{2-}$  ions [13].

It is known [14–22] that aluminum and its alloys can be in a passive state, however, they can undergo local activation (LA) in the presence of chloride, sulfate, nitrate, and other ions. Yet, there is hardly any information about the behavior of aluminum and its alloys in the presence of bicarbonate ions. Papers [23–24] describe studies on the effect of temperature on aluminum LA in  $\text{NaHCO}_3$  solutions. It was also shown that at concentrations of  $10^{-5}$ – $10^{-4} \text{ M}$  and  $5 \cdot 10^{-5}$ – $10^{-1} \text{ M}$  of  $\text{NaHCO}_3$ , aluminum is in a passive state, while at concentrations between  $2 \cdot 10^{-4}$  and  $4 \cdot 10^{-3} \text{ M}$ , there is LA in  $\text{NaHCO}_3$ . Controversial behavior of aluminum [23–24], as well as different views [6–12] on the role of pH of bicarbonate solutions and  $\text{HCO}_3^-$  ions in the LA processes on metals with low salt content in the solution means that there is a need for a more detailed study in a wide range of potentials, clarification of the concentration boundaries of LA and its kinetic parameters, and determination of the mechanism of the process of aluminum LA in bicarbonate media. Therefore, the purpose of the article is to study the effect of bicarbonate ions on the local activation of aluminum at a temperature of 25 °C.

## 2. Experimental

Experiments were carried out on a stationary aluminum (Al 99.99%) electrode in aqueous solutions of sodium bicarbonate within the concentration range from  $2 \cdot 10^{-4}$  to  $4 \cdot 10^{-3} \text{ M}$ , which were prepared from a chemically pure reagent and distilled water and which were kept for a day. The pH control of the studied solutions (PH-107 pH meter with an accuracy of 0.1) showed a change in the pH value from 6.5 to 7.7 with an increase in the salt content of the electrolytes.

Prior to each experiment, the aluminum surface was polished with sandpaper with a decreasing grain radius, polished with filter paper, degreased with ethanol, and washed with distilled water.

The electrolytic cell was a glass three-electrode cell with unseparated cathode and anode spaces and free access of air. The working (aluminum) and auxiliary platinum electrodes

and a salt bridge tube were fixed in the cell lid. A silver chloride electrode ( $E = 0.20$  V) was used as the reference electrode. It was located in the salt bridge, which was filled with a working solution at room temperature and had a Haber-Luggin capillary at its end. All potentials were further recalculated relative to the standard hydrogen electrode [25–28].

The anodic behavior of aluminum in the corresponding  $\text{NaHCO}_3$  solutions was studied at room temperature on an IPC-Compact potentiostat using Equivalent Circuits Solver software (Ver 1.2) (accuracy  $\pm 0.002$  V).

Linear sweep voltammetry was chosen as the main electrochemical method of the study. To use it, at the beginning of each experiment, the electrode was placed in the working solution and kept in it for 10 minutes. Then, the anodic polarization curve (APC) of the steady-state potential was taken (scanning rate of  $v_p = 0.15$  V/min). The electrode potential was shifted sequentially to the region of positive values up to  $E = +1.00$  V. For quantitative evaluation of the stage of the PT initiation, we used the potential of pitting formation ( $E_{\text{PF}}$ ), i.e. the critical value of the potential, more positive values of which are associated with the activating effect of anions. The approximate  $E_{\text{PF}}$  was determined by the potential corresponding to the sharp increase in the anodic current on the APC [29–31].

Additional studies were carried out by chronoamperometry, within which the shape of kinetic  $I - \tau$  curves at fixed potential values were used to draw conclusions about the state of the studied metal: whether it was being actively dissolved, passivated, or exposed to LA. Importantly, the quantitative characteristic of LA was the LA potential ( $E_{\text{LA}}$ ), which corresponded to the potential associated with the formation of the first metastable PT, the further development or repassivation of which was determined by a number of factors: the conditions of the experiment, the nature of the metal and the activator, the temperature, and the rate of PT formation. To obtain chronoamperograms, the surface of the electrode was treated as described above prior to each experiment. Then, the electrode was kept in the working solution for 10 min. After that, the sample was anodically

polarized at different potential values around  $E_{\text{LA}}$ . After that, the change in the current over time was recorded for 10 minutes every 10 seconds. The obtained chronoamperometric data were compared with visual (microscopic) observations [32–34].

The combination of voltammetric and chronoamperometric methods was necessary in this case, since, as a rule,  $E_{\text{LA}}$  and  $E_{\text{PF}}$  did not agree with each other, and usually  $E_{\text{LA}} < E_{\text{PO}}$ .

When studying the stage of PT initiation, the concept of the induction period of PF or LA ( $\tau_{\text{ind}}$ ) is often used [33, 35], which, depending on the accepted theory of metal passivity, is understood as the time required for the penetration of the activator ion through the oxide film (film theory), or for successful competitive adsorption between the passivator and the activator in favor of the latter (adsorption theory) [28, 35]. The  $\tau_{\text{ind}}$  value depends not only on the nature of the metal, the composition of the solution, the type of activator, its concentration, pH, the presence of foreign substances, and temperature, but also on the potential of the electrode. This indicates [32, 33, 35] that the  $\tau_{\text{ind}}$  value can be interpreted as a characteristic proportional to the reaction rate responsible for the appearance of PT. The  $\tau_{\text{ind}}$  value was determined according to the following procedure. After mechanical treatment of the electrode surface and immersing it for 10 minutes in the solution, the sample was exposed to anodic polarization in the solution at a potential corresponding to the potential of stable LA. The start time of the electrode activation,  $\tau_{\text{ind}}$ , was recorded, which corresponded to the start of fluctuations of the anodic current or its sharp increase [31, 36].

Electrochemical measurements were supplemented with visual control of the state of the working surface of the electrode before and after each experiment (voltammetry, chronoamperometry) using MBS-2 (at magnification of  $\times 7$ ) and MIM-7 (at magnification of  $\times 500$ ) microscopes. The intensity of aluminum LA in the working solutions was determined by the shape, diameter, and depth of the PT and its concentration on the surface. The depth of the PT was established by the method of double focusing using the micrometric screw of the MIM-7 microscope. The method involved

alternate focusing of the optical system on the inner surface of the PT and on the smooth surface of the metal [37]. The diameter was determined using the eyepiece reticle of the MIM-7 microscope. The destruction of the metal surface was photographed with a digital camera. The surface morphology of the working electrode was determined by the SEM method. For this, the analyzed sample was placed in a cuvette in the working chamber of the JSM-6510 LV scanning electron microscope and then the corresponding micrographs were taken.

The elemental composition of the products formed during the electrochemical studies was determined using X-ray spectral microanalysis on the BRUKER 129 eV energy dispersive attachment to the JSM-6510 LV scanning electron microscope.

### 3. Results and discussion

Electrochemical studies of the aluminum behavior in bicarbonate solutions allowed establishing the region of metal LA corresponding to the concentration range of  $2 \cdot 10^{-4}$ – $4 \cdot 10^{-3}$  M. Beyond this range, aluminum remained in a passive state [23–24]. The results of the study showed that the LA region is characterized by both a change in the shape of the anodic polarization curves (Fig. 1) and nonmonotonic dependencies of the main quantitative characteristics of the LA process ( $E_{PF}$ ,  $E_{LA}$ , and  $\tau_{ind}$ ) on the concentration of bicarbonate ions.

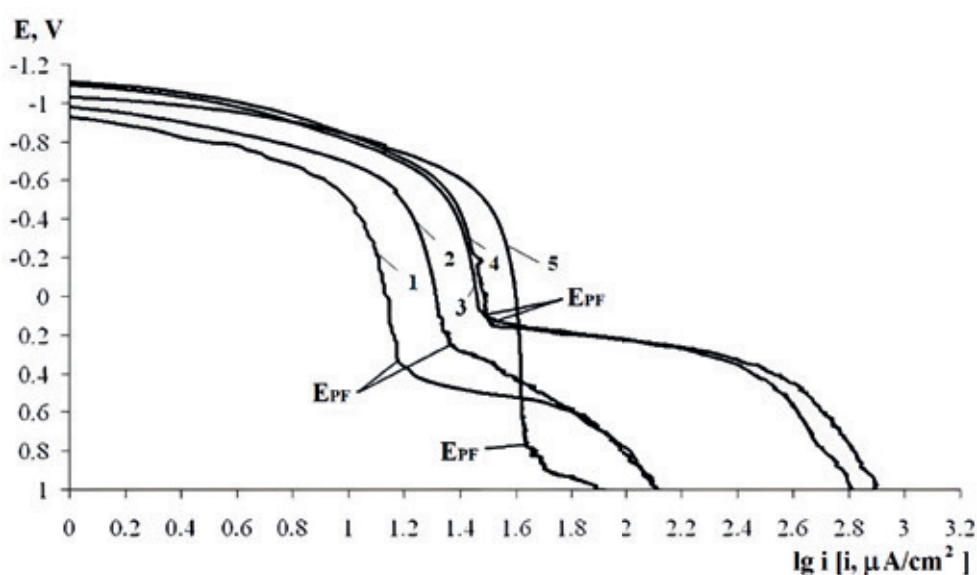
In the range from  $2 \cdot 10^{-4}$  M to  $4 \cdot 10^{-3}$  M,  $E_{PF}$  on the APC varied from 0.165 V (in a solution of  $2 \cdot 10^{-4}$  M  $\text{NaHCO}_3$ ) to 0.766 V (in a solution of  $4 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ ) (Table 1). Moreover, after APC was taken, localized damage was observed on the surface of aluminum, i.e. PT, the diameter ( $d$ ) and height ( $h$ ) of which decreased with an increase in the concentration of  $\text{HCO}_3^-$  ions (Table 1).

Breakdown of metal passivity in the studied systems was also confirmed by characteristic fluctuations on the corresponding chronoamperograms taken at  $E_{LA}$  (Fig. 2).

According to the chronoamperograms, pitting damage on the surface of aluminum at  $E_{LA}$  did not occur immediately, but only after some  $\tau_{ind}$  (Fig. 2), the value of which increased considerably with an increase in the concentration of  $\text{NaHCO}_3$  from  $2 \cdot 10^{-5}$  to  $4 \cdot 10^{-3}$  M. The opposite effect was observed in solutions of  $2 \cdot 10^{-4}$ – $2 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ , where the value of  $\tau_{ind}$  decreased with an increase in salt content.

What is more,  $E_{LA}$  was first gradually shifted to the negative region from 0.180 V (at  $2 \cdot 10^{-4}$  M  $\text{NaHCO}_3$ ) to  $-0.020$  V (at  $2 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ ), and then it began to increase sharply to 0.600 V (at  $4 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ ) (Table 1).

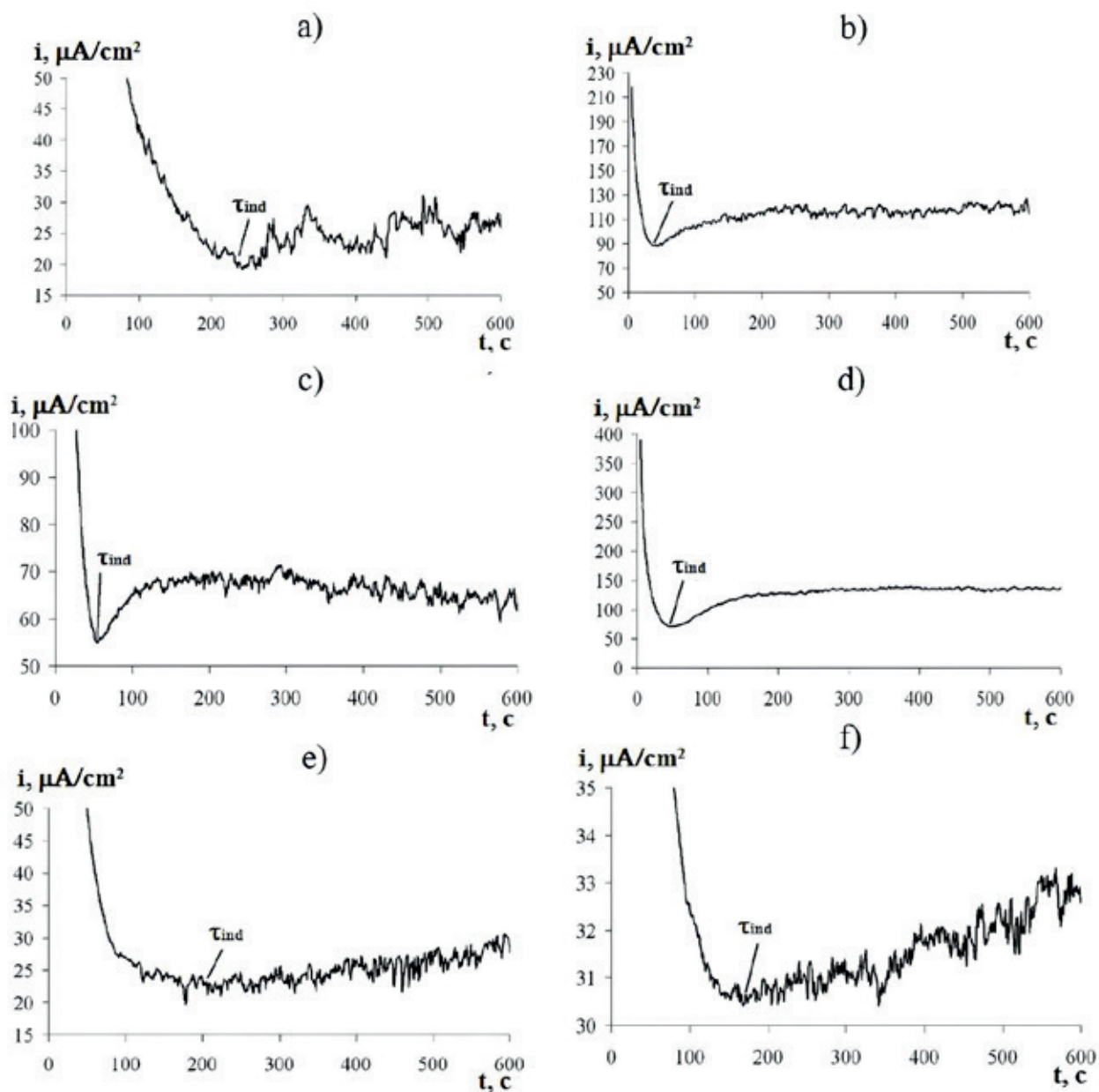
For a more detailed study of the morphology of the aluminum surface, an additional study was carried out using the SEM and PCM methods. The latter was used to determine the quantitative



**Fig. 1** APC for aluminum in  $\text{NaHCO}_3$  solution with concentrations of  $5 \cdot 10^{-4}$  (1),  $1 \cdot 10^{-3}$  (2),  $2 \cdot 10^{-3}$  (3),  $3 \cdot 10^{-3}$  (4),  $4 \cdot 10^{-3}$  (5) M ( $v_p = 0.15$  V/min,  $T = 25 \pm 2^\circ$  C)

**Table 1.** Quantitative characteristics of the process of aluminum LA in  $\text{NaHCO}_3$  solutions

The concentration of $\text{NaHCO}_3$ , M	pH before/pH after the experiment	$E_{\text{pp}}$ , V	$E_{\text{LA}}$ , V	$\tau_{\text{ind}}$ , s	Depth $h$ , $\mu\text{m}$	Diameter $d$ , $\mu\text{m}$
$2 \cdot 10^{-4}$	6.5/6.5	0.165	0.180	155	6	10
$5 \cdot 10^{-4}$	6.8/6.8	0.340	0.080	40	6	10
$1 \cdot 10^{-3}$	7.2/7.2	0.260	0.060	53	6	10
$2 \cdot 10^{-3}$	7.4/7.4	0.0830	-0.020	32	<3	5
$3 \cdot 10^{-3}$	7.4/7.4	0.150	-0.020	202	<3	5
$4 \cdot 10^{-3}$	7.7/7.7	0.766	0.600	228	<3	5


**Fig. 2** Chronoamperograms for aluminum in  $\text{NaHCO}_3$  solution at: a)  $C = 2 \cdot 10^{-4}$  M and  $E = 0.18$  V; b)  $C = 5 \cdot 10^{-4}$  M and  $E = 0.08$  V; c)  $C = 1 \cdot 10^{-3}$  M and  $E = 0.06$  V; d)  $C = 2 \cdot 10^{-3}$  M and  $E = -0.02$  V; e)  $C = 3 \cdot 10^{-3}$  M and  $E = -0.02$  V; f)  $C = 4 \cdot 10^{-3}$  M and  $E = 0.60$  V

content of chemical elements present in the film on the metal surface before (Table 2) and after (Tables 3 and 4) the electrochemical experiments. After that, comparative studies of the PT region (Tables 3a and 4a) and the metal surface without localized damage (Tables 3b and 4b) were carried out.

**Table 2.** Elemental composition of the film (in the selected region) on the surface of aluminum before voltammetric studies at 25 °C and their quantitative ratio

X-ray structural microanalysis		Surface micrography (SEM)
Element	Weight %	
Al	70.38	
O	7.20	
Si	14.17	
C	8.25	

According to the data obtained before the electrochemical experiments, the following elements were present on the aluminum surface: Al, O, Si, and C (Table 2). After the APC was taken, the following elements were found on the aluminum surface in the solutions of  $1 \cdot 10^{-3}$  M and  $4 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ : Al, O, C, Na, Si, and Mg (the weight percentage of the corresponding element given in Tables 3–4 corresponded to the location of the selected band on the metal). The ratio of the weight percentage of Al and O elements related to the thickness of the film formed on the metal surface was of particular interest [6, 18, 26]. For example, the total film thickness after voltammetric studies (Tables 3b and 4b) was almost 2 times greater as compared to the original surface (Table 2).

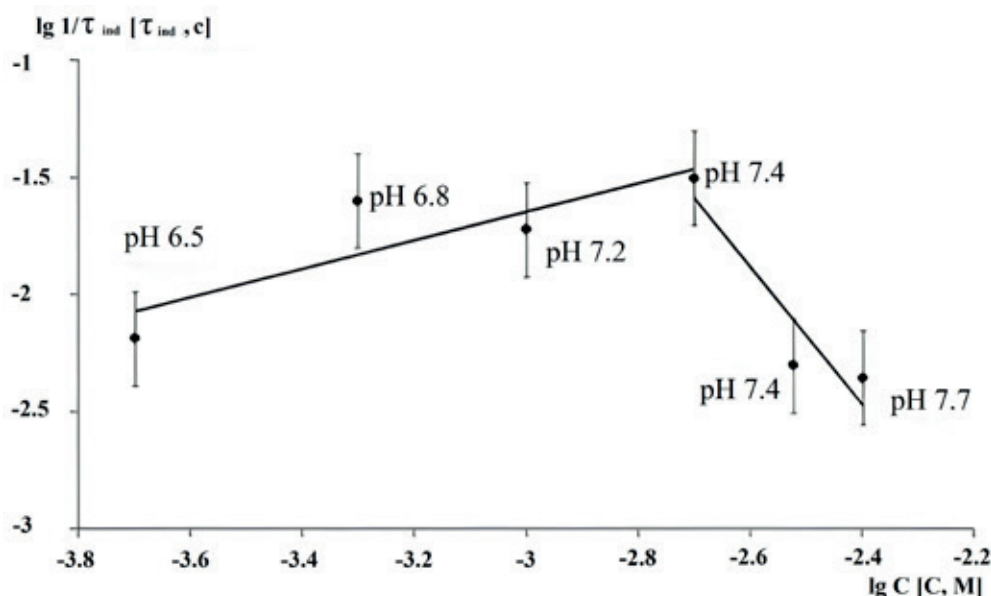
Following the formal kinetic approach [21, 22], to assess the control stage of the PF process, the LA region was divided into two regions ( $n_1 = 0.60$  ( $C_{\text{NaHCO}_3} = 2 \cdot 10^{-4} - 2 \cdot 10^{-3}$  M) and  $n_2 = -2.94$

**Table 3.** Elemental composition of the film (in the selected region) on the surface of aluminum after voltammetric studies in a solution of  $1 \cdot 10^{-3}$  M of  $\text{NaHCO}_3$  (in PT (a) and in the film on the surface (b)) at 25 °C, and their quantitative ratio

X-ray structural microanalysis		Surface micrography (SEM)	X-ray structural microanalysis		Surface micrography (SEM)
Element	Weight %		Element	Weight %	
a) In the PT			b) In the surface film		
Na	0.53		Na	0.30	
Al	82.43		Al	75.52	
C	7.06		C	7.62	
O	8.92		O	15.33	
Si	0.67		Si	0.94	
Mg	0.39		Mg	0.29	

**Table 4.** Elemental composition of the film (in the selected region) on the surface of aluminum after voltammetric studies in a solution of  $4 \cdot 10^{-3}$  M of  $\text{NaHCO}_3$  (in PT (a) and in the film on the surface (b)) at 25 °C, and their quantitative ratio

X-ray structural microanalysis		Surface micrography (SEM)	X-ray structural microanalysis		Surface micrography (SEM)
Element	Weight %		Element	Weight %	
a) In the PT			b) In the surface film		
Na	0.29		Na	0.09	
Al	39.32		Al	79.88	
C	47.81		C	4.81	
O	11.45		O	14.23	
Si	0.68		Si	0.99	
Mg	0.45		Mg	0.99	



**Fig. 3** Influence of  $\text{NaHCO}_3$  concentration and pH on the rate of the process of aluminum LA ( $C_{\text{NaHCO}_3} = 2 \cdot 10^{-4}$ – $4 \cdot 10^{-3}$  M,  $T = 25 \pm 2$  °C)

( $C_{\text{NaHCO}_3} = 2 \cdot 10^{-3}$ – $4 \cdot 10^{-3}$  M)), at the boundary of which the PF mechanism probably changed (Fig. 3). In this case, the value of  $n$  is the apparent kinetic order of the reaction for the aggressive ion, and  $1/\tau_{\text{ind}}$  is the rate of PT initiation [13, 33, 35]:

$$n_{\text{HCO}_3^-} = d \lg(1/\tau_{\text{ind}}) / d \lg C_{\text{HCO}_3^-} \quad (2)$$

The fractional reaction orders obtained during the studied process (Fig. 3) were associated with the accuracy of determining the induction period. The type of adsorption isotherm of ions involved in the PF and PT repassivation processes or the proportion of the actual surface of the localized damage on aluminum were mainly not taken into consideration.

It was shown that with an increase in the concentration of  $\text{NaHCO}_3$ , the rate of PT initiation ( $1/\tau_{\text{ind}}$ ) first increased ( $n_1$ ) and then decreased ( $n_2$ ) (Fig. 3).

In accordance with previous studies, in particular conducted within the adsorption theory and the model of nucleophilic substitution model [22, 35, 38–41], we proposed the following mechanism for the observed phenomenon.

In the range of  $\text{NaHCO}_3$  concentrations from  $2 \cdot 10^{-4}$  to  $2 \cdot 10^{-3}$  M (pH = 6.5–7.4) and  $n_1 = 0.60$ , the passivating film has low protective characteristics, and  $\text{HCO}_3^-$  ions act as activators of pitting corrosion and cause aluminum depassivation as follows:

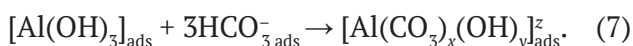


Since the apparent kinetic order of the process for  $\text{HCO}_3^-$  ion is  $n = 0.60$  (i.e. close to an integer value of 1) (Fig. 3), the limiting stage of the process is most likely the association of the  $[\text{Al}(\text{OH})_3]_{\text{ads}}$  complex with bicarbonate ions (4).

The formed compounds  $[\text{Al}(\text{HCO}_3)_3]_{\text{ads}}$  are unstable, since they are formed by a weak base and a weak acid and probably further decompose and pass into the bulk electrolyte (5). This mechanism is confirmed by the formation of open PT on aluminum in this LA region, which is clearly visible in the SEM photographs (Table 3a). PCM method, which was also used, allowed to establish that the ratio of the weight percentage of Al and O elements in the PT corresponded to the original surface (Tables 2 and 3a).

With an increase in the concentration of  $\text{HCO}_3^-$  ions from  $2 \cdot 10^{-3}$  to  $4 \cdot 10^{-3}$  M (pH = 7.4–7.7) and  $n_2 = -2.94$ , the protective properties of the oxide film in relation to the PF increased, the LA process was inhibited, and the PT diameter and depth decreased (Table 1), which was explained by the stabilization of the passive film on aluminum as follows:





SEM photographs were used to prove the proposed mechanism (Table 4a). They clearly showed that in the second LA region PT formed under a “cap” of an insoluble compound. Moreover, according to the PCM data, PT (Table 4a) had a high (in comparison with the initial surface (Table 2)) content of O and C elements and low content of Al. In accordance with previous studies [42], for example, dawsonite  $\text{NaAlCO}_3(\text{OH})_2$  can be classified as such insoluble salt (8). However, more research is needed to establish the exact formula of the chemical compound formed on the surface of aluminum.

#### 4. Conclusions

A set of independent physicochemical methods were used to determine the concentration boundaries of the area of localized destruction of aluminum in bicarbonate media ( $2 \cdot 10^{-4}$ – $4 \cdot 10^{-3}$  M  $\text{NaHCO}_3$ ), to obtain systematic experimental data on the dependence of the main quantitative characteristics of the LA process ( $E_{\text{pf}}$ ,  $E_{\text{LA}}$ , and  $\tau_{\text{ind}}$ ) on the concentration of sodium bicarbonate. It was shown that  $\text{HCO}_3^-$  ions can exhibit a dual nature, causing both activation and inhibition of the LA process depending on the concentration of bicarbonate ions. During the study, in accordance with the formal kinetic approach, to assess the control stage of the pitting formation process, the LA region was divided into two regions:  $2 \cdot 10^{-4}$ – $2 \cdot 10^{-3}$  M and  $2 \cdot 10^{-3}$ – $4 \cdot 10^{-3}$  M of  $\text{NaHCO}_3$  concentrations with the reaction order  $n_1 = 0.60$  ( $C_{\text{NaHCO}_3} = 2 \cdot 10^{-4}$ – $2 \cdot 10^{-3}$  M) and  $n_2 = -2.94$  ( $C_{\text{NaHCO}_3} = 2 \cdot 10^{-3}$ – $4 \cdot 10^{-3}$  M), respectively. The adsorption theory and the model of nucleophilic substitution were used to propose the mechanisms of aluminum LA in hydrocarbonate media. The limiting stage of the process in the first LA region is the stage of association of the  $[\text{Al}(\text{OH})_3]_{\text{ads}}$  complex with bicarbonate-ions. In the second LA region, an insoluble compound of complex composition is formed (the general formula of which is probably  $[\text{Al}(\text{CO}_3)_x(\text{OH})_y]_{\text{ads}}^z$ ) in a shape of a “cap” over the pitting. It was shown that the mechanism of the process of aluminum LA changes at a concentration of  $2 \cdot 10^{-3}$  M of  $\text{NaHCO}_3$ , which is associated with a change in the solubility and nature of the compounds forming the protective film. Further research should be aimed

at studying the adsorption of bicarbonate ions on passive metal and should take into consideration the type of its isotherms.

#### Contribution of the authors

T. A. Minakova: text writing, study of literature, development of methodology, and final conclusions. S. A. Kaluzhina: scientific supervision, research concept, text editing, E. N. Aksyonova: conducting research.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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