

## **Inhibition of bismuth dissolution in 0.1 M sodium chloride solution**

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### **Abstract**

Some organic compounds were studied as inhibitors of bismuth dissolution in passive state and under depassivation conditions in 0.1 M sodium chloride solution. The relationship between the effects of the organic additive and the  $\text{Cl}^-$  ion was estimated. Information about the influence of additives on the rate-limiting step under potentiostatic polarization was obtained.

**Key words:** *inhibitors, bismuth, anodic dissolution, sodium chloride solution, passivation, depassivation, mass transfer.*

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### **Introduction**

Of additives in anodic dissolution of bismuth in neutral media, inorganic anions have been studied most thoroughly [1, 2]. Literature data on the influence of organic additives are confined to dissolution in sulfate [3] and borate solutions. It seemed expedient to determine some regularities of the effect of organic additives of various types on the anodic behavior of bismuth in chloride solution.

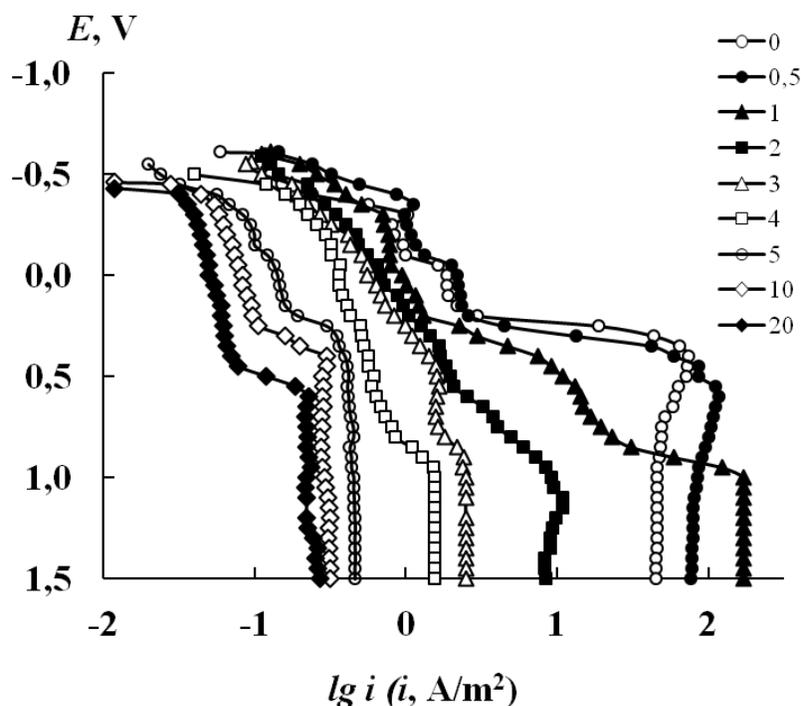
### **Experimental procedure**

The electrode preparation and the experiment were carried out according to traditional procedures. 1,2,3-Benzotriazole (BTA), 9-aminoacridine hydrochloride (AAH), potassium oleate (PO), 8-quinolinol and sodium phenylanthranilate, which are known as rust and anodic dissolution inhibitors of a number of metals in neutral media, were used as the additives. Their efficiency was estimated by inhibition factor  $\gamma$ , which is the ratio of the process rates in the pure solution and with an additive, as well as by the characteristic potential difference  $\Delta E$  in solutions with and without an additive. Sodium chloride free solutions of organic compounds were used for comparison.

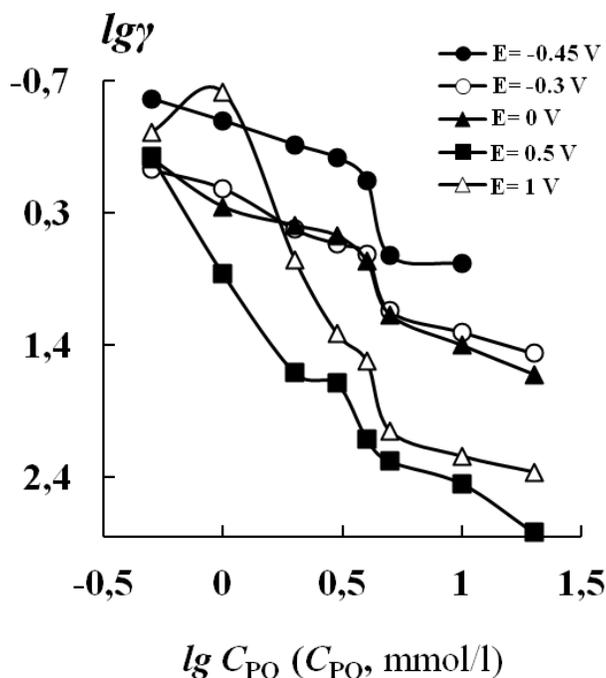
### **Results and discussion**

According to polarization measurement data, the pattern and value of oleate effect depend essentially on its concentration  $C_{\text{PO}}$  and potential  $E$  (Fig. 1). Oleate accelerates dissolution before the first and after the second peak at small  $C$ . At other  $C$  and  $E$  values, it behaves as

an inhibitor whose protective effect increases with  $C_{PO}$ . This pattern of  $C_{PO}$  effect on  $\Delta E$  and  $\gamma$  (Fig. 2) gives ground for separating the solutions into two groups with a boundary  $C_{PO} \approx 4$  mmol/l. In both groups, the dependences are quite similar, but differ in slope and/or are biased relative to each other.



**Figure 1.** Forward anodic polarization curves in 0,1 M solution of NaCl depending on  $C_{PO}$ , mmol/l.



**Figure 2.**  $\lg \gamma - \lg C_{PO}$  plots of at some  $E$  values.

One of the reasons of the existence of these two groups of solutions may lie in the change of oleate function with an increase in concentration. In the first group, at  $C_{PO} < 3$  mmol/l, the leading role apparently belongs to a film consisting of  $\text{Bi}_2\text{O}_3$  and basic salts, while oleate either principally prevents its formation at smaller concentrations or increases its protective properties at higher ones. The latter is possible due to formation of hardly soluble compounds with  $\text{Bi}^{3+}$  or an increase in protective capability upon influence of the surface active anion on the film structure. In these solutions, in comparison with those containing only chloride, the film is more easily removed from the surface, large pits disappear. However, as  $C_{PO}$  increases, the depth of small pits increases, while light reflected from the surface is shifted to the short-wave region from blue-green to indigo-blue by  $C_{PO} = 5$  mmol/l. The latter fact indicates that the film becomes thinner and, accordingly, its protective properties increase.

It can be believed that in the second group of solutions, the main part is played by adsorbed oleate or a very thin film of bismuth oleate. In fact, at  $C_{PO} \geq 10$  mmol/l the electrode surface retains its metal luster, and pits are not detected visually under 10x magnification. This might suggest adsorption passivation by oleate; however, as demonstrated below, a film does exist.

Film thinning upon oleate addition is confirmed by the reverse polarization curve recorded after a forward curve is taken up to  $E = 0.1$  V. Oleate preserves a protective effect as the potential is decreased during the reverse anodic curve; at  $C_{PO} = 10$  mmol/l,  $\gamma = 8.2–9.5$ . Moreover, it increases the zero-current potential  $E_{i=0}$  by 120 mV and decreases the potentials of the two cathodic peaks by 70 mV and reduces their currents by a factor of 2.5. The change in  $E_{i=0}$  allows us to assume a change in the passive film composition in the oleate solution.

Anodic chronoamperograms in chloride solutions containing oleate in characteristic coordinates  $i^{-1} - \tau^{1/2}$  consist of two segments. One of these describes the processes which occur under diffusion-kinetic control and are described by equation (1). For the other one,  $p \approx 0$ , which indicates the diffusion nature of the process (Table 1).

$$i^{-1} = p + \lambda^{-1} \tau^{1/2} \quad (1)$$

As usual, the diffusion-kinetic behavior precedes the diffusion behavior in dilute oleate solutions. An increase in  $C_{PO}$  shortens the time of the transition, and at  $C_{PO} = 10$  mmol/l, non-steady-state diffusion limits the process almost at once. In this solution, after a while, the straight line goes more steeply due to an improvement in the film protective properties, while  $\lambda$  and, correspondingly, the effective diffusion coefficient decrease. In the second segment,  $p < 0$  and equation (1) takes the form:

$$i^{-1} = \lambda^{-1}(\tau^{1/2} - \tau_0^{1/2}) \quad (2)$$

where the incubation period is  $\tau_0 = (-p \cdot \lambda)^2 = 16$  s.

**Table 1.** Dependence of chronoamperogram characteristics at  $E = 0.1$  V, correlation factor  $R$  and  $\gamma_{\text{chag}}$  on  $C_{\text{PO}}$ .

$C_{\text{PO}}$	$p, \text{m}^2/\text{A}$	$\lambda, \text{A s}^{0.5} \text{m}^2$	$R$	Time interval, s	$q_{\text{chag}}, \text{kC}/\text{m}^2$	$\gamma_{\text{chag}}$
0	0.024	91	0.994	2–900	3.6	–
1	0.081	77	0.994	Less than 240	2.6	1.4
	0.003	62	0.970	More than 260		
3	0.096	52	0.991	Less than 180	0.9	4.0
	–0.006	38	0.998	More than 240		
10	0.007	17	0.999	Less than 120	0.7	5.1
	–3.625	4.5	0.999	More than 480		

Note.  $\gamma_{\text{chag}}$  is the inhibition ratio indicating the factor of reduction of charge  $q_{\text{chag}}$  by oleate, *i.e.*, the mean dissolution rate over 900 seconds.

Cathodic chronoamperograms at  $C_{\text{PO}} = 1$  mmol/l taken after anodic chronoamperograms show only the second delay at the same potential  $E_{\text{d}} = -0.75$  V. However, the delay time is two times smaller than in the pure solution. An increase in  $C_{\text{PO}}$  to 3 mmol/l again decreases the time at this  $E_{\text{d}}$  twofold but produces a second, more prolonged delay at  $E_{\text{d}} = -0.85$  V. Finally, at  $C_{\text{PO}} = 10$  mmol/l, one delay with  $E_{\text{d}} = -0.95$  V and about  $0.4 \text{ kC}/\text{m}^2$  charge occurs, which constitutes 57% of  $q_{\text{chag}}$ . It shows that the fraction of current consumed for phase formation in potentiostatic mode is eight times higher than in the pure solution, and the resultant film shows higher protective properties.

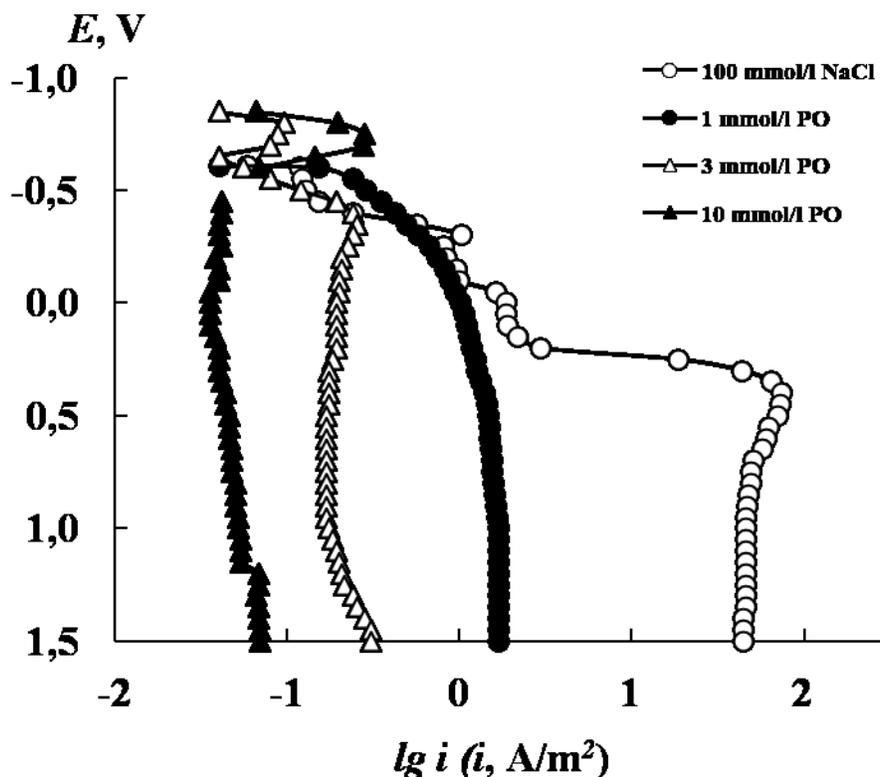
In 0.01 M potassium oleate solution free of sodium chloride, the main regions of the anodic chronoamperogram are similar to those obtained in 0.1 M sodium chloride solution. The  $\alpha$  values show that the rates of dissolution and its stages at  $E = 0.1$  V are considerably lower in the former case (Table 2).

**Table 2.** Chronoamperogram characteristics at  $E=0.1$  V in 0.01 M potassium oleate solution and the  $R$  and  $\alpha$  values.

$p, /\text{A}$	$\alpha_p$	$\lambda, \text{A s}^{0.5} \text{m}^2$	$\alpha_\lambda$	$R$	Time interval, s
0.13	0.18	9.1	10	0.991	2–900
0.23	0.13	11	7.6	0.996	2–230
0.001	–	8.8	8.2	0.996	250–600
–1.59	0.35	5.5	6.7	0.995	620–900

Note. For time range of 620–900 s,  $\tau_0 = 78$  s. For the entire range,  $q_{\text{chag}} = 0.5 \text{ kC}/\text{m}^2$ .  $\alpha$  is the ratio of  $p$  or  $\lambda$  in chloride and oleate solutions. As  $p$  is the reciprocal of the rate of the charge transfer stage, the values  $\alpha_p < 1$  mean a decrease in this rate.

In oleate solutions,  $E_{\text{cor}}$  significantly decreases in comparison with chloride solutions and anodic peaks occur (Fig. 3). It can be a consequence of cathodic reaction hindrance by the additive, and in such case, most probably, the peak corresponds to the formation of  $\text{Bi}_2\text{O}_3$ . However, cathodic curves at  $C_{\text{PO}} = 1 \text{ mmol/l}$  and  $E < -0.8 \text{ V}$  show that the additive has no effect. This potential, just as  $E_{\text{cor}}$ , decreases along with  $C_{\text{PO}}$  increase. Besides, based on Nernst equation for bismuth oxide electrode, pH of the near-electrode layer should increase to 15.6 to ensure  $\text{Bi}_2\text{O}_3$  formation, but this does not occur. Thus, the decrease in the cathodic current with an increase in  $C_{\text{PO}}$  on approaching  $E_{\text{cor}}$  can be logically related to acceleration of the anodic reaction by oleate. Then, the peak is due to formation of bismuth oleate, and the subsequent decrease in the metal dissolution rate provides a cathodic current loop at  $C_{\text{PO}} = 10 \text{ mmol/l}$  to which the anodic curve discontinuity refers. In these curves, unlike those recorded in chloride solutions, there are no areas of step-by-step passivation-activation (Figs. 1, 3). Yet, an increase in current after the anodic peak at  $C_{\text{PO}} = 3\text{--}10 \text{ mmol/l}$  or after  $E_{\text{cor}}$  at  $C_{\text{PO}} = 1 \text{ mmol/l}$  is followed by local surface damage. The number and diameter of pits decrease with an increase in  $C_{\text{PO}}$ . Hence, oleate acts both as a passivator and depassivator in these solutions. Unlike chloride solutions containing oleate, the surface loses metallic luster and becomes opaque-grey after the experiment.



**Figure 3.** Anodic polarisation curves in chloride and oleate solutions.

Comparison of the curves recorded in chloride, oleate, and chloride–oleate solutions (Figs. 1, 3) shows that in the latter two solutions at  $C_{\text{PO}} = 1 \text{ mmol/l}$ , the activating effect of oleate predominates below  $E_{\text{a},1}$  whereas the inhibiting effect predominates from  $E_{\text{a},1}$  to  $E_{\text{a},3}$ .

At large potentials it becomes lower but persists, and as a consequence, depassivation occurs in two stages. At  $C_{PO} = 3$  mmol/l, the curves from  $E_{cor}$  to  $E = -0.4$  V are almost the same in the three solutions, and subsequently, the activating effect of chloride in oleate solution and the inhibiting effect of oleate in chloride solution are comparable. At  $C_{PO} = 10$  mmol/l, the hindering effect of oleate prevails in all segments of the curve in chloride solution containing the additive.

The currents in benzotriazole solutions are larger than in oleate solutions, while the efficiency of this additive is smaller than that of oleate and weakly depends on  $C$  (Figs. 1, 3, 4). Benzotriazole preserves the step-like character of the anodic curve in a broader range of concentrations. Change in concentration changes the efficiency of the additive in rather a specific way. On the other hand, some generalizations can be made. Benzotriazole prevents oxide passivation almost at any concentrations. That is why the region passive state due to  $Bi_2O_3$  formation is not observed on the anodic curve. Based on the character of concentration dependence of benzotriazole effect on the anodic reaction, the interval of potentials studied is divided into two groups. In most cases, the plots of  $\Delta E$  and  $\gamma$  on  $C_{BT}$  below  $E_{a,3}$  have an extremum close to  $C_{BT} = 1-2$  mmol/l. This behavior is usually typical of additives that form complexes with metal cations. At large potentials in the limiting diffusion current domain, the efficiency of benzotriazole is minor and monotonously changes from weak stimulation up to weak inhibiting action with an increase in benzotriazole concentration (Table 3).

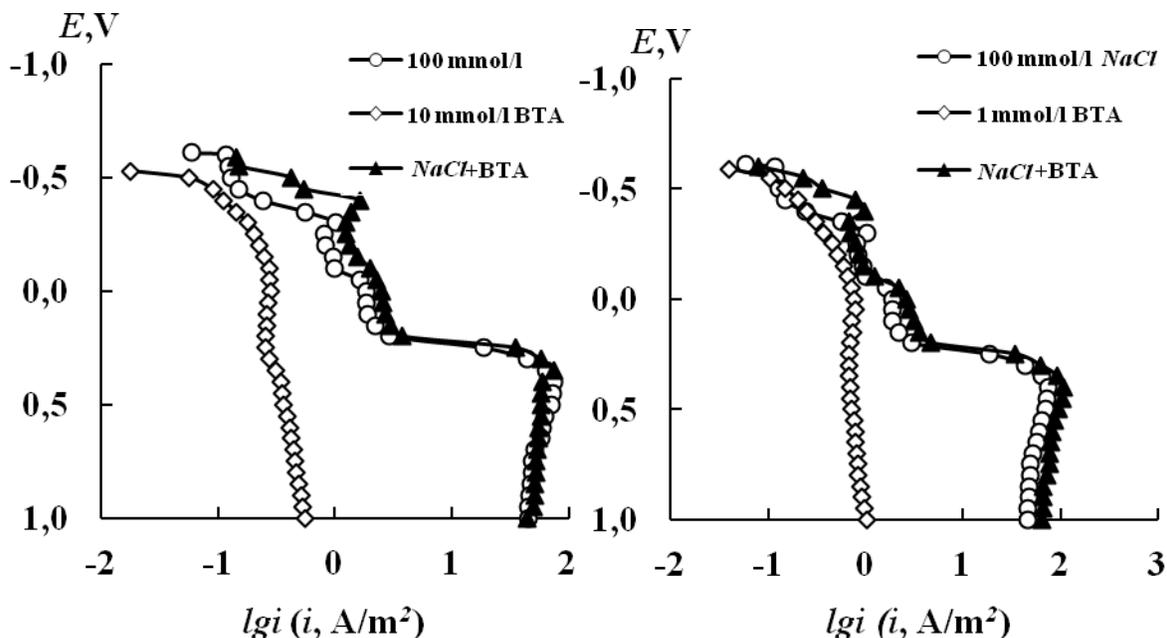
**Table 3.** Concentration dependence of benzotriazole efficiency.

$C_{BTA}$	$\Delta E_{cor}$	$-\Delta E_{ad,1}$	$\gamma_{ad,1}$	$\gamma$ values at E, V			
				-0.45	-0.30	0.10	0.70
0.5	0	0.05	1.52	0.79	1.55	0.93	0.90
1	-0.05	0.10	1.46	0.27	2.04	0.81	0.94
2	0.04	0.15	0.69	0.11	1.23	1.13	1.04
5	0.02	0.10	0.78	0.40	0.97	1.03	1.07
10	0.04	0.10	0.85	9.58	1.12	0.95	1.29
20	0.10	0.10	0.80	2.22	2.14	0.82	1.32

*Note.*  $\Delta E_{ad,1}$  is the change in the first anodic peak potential;  $\gamma_{ad,1}$  shows the effect of the additive on the current of that peak.

In all these solutions, the surface after the experiment is coated with a loose film with weak adhesion. At small  $C_{BTA}$  values, approximately five larger corrosion sites and plenty of little ones per  $1\text{ cm}^2$  of the surface are observed. With  $C_{BTA}$  increase the former almost disappear, while the number of the latter decreases significantly. In chloride-free benzotriazole solutions, the anodic curve has a simpler form with one peak. Below  $E_{ap,1}$ , the

process rate in benzotriazole and NaCl solutions is higher than in NaCl solution with benzotriazole additive. The activating effect of chloride prevails at larger potentials (Fig. 4).



**Figure 4.** Anodic polarization curves in chloride, benzotriazole and chloride + benzotriazole solutions.

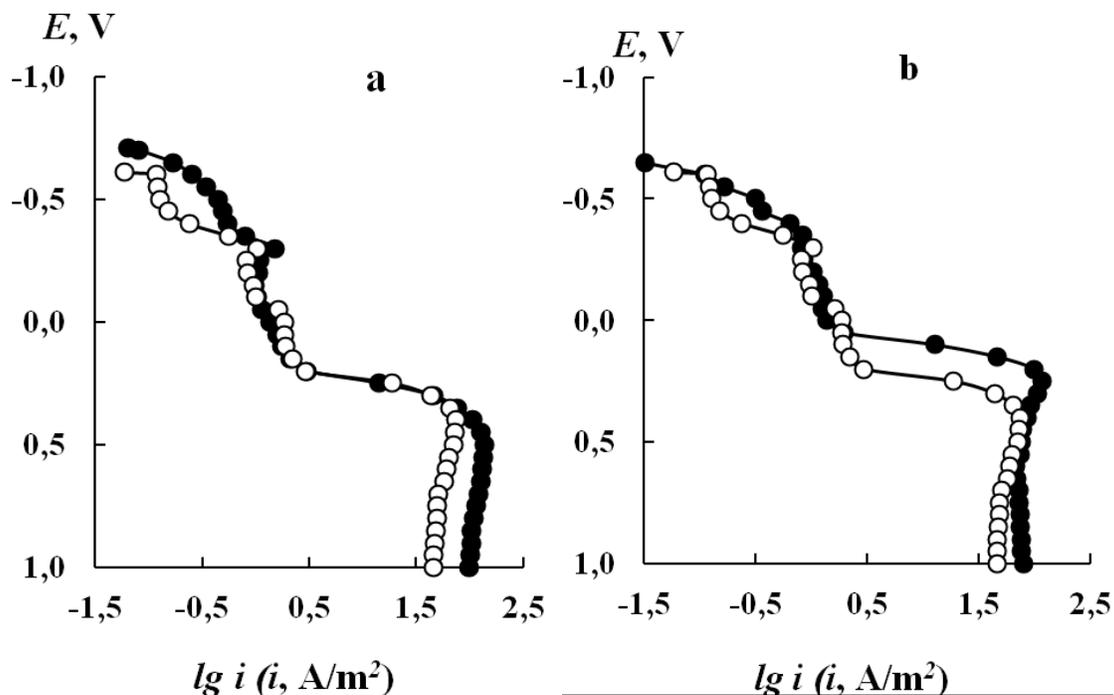
The effects of aminoacridine and benzotriazole are similar in many ways. AAH prevents oxide passivation, although this region is retained, reduces the passive dissolution current due to basic salt formation, does not change  $E_{a,3}$  much and slightly increases the subsequent limiting anodic current. However, unlike benzotriazole, aminoacridine nearly does not change the coordinates of the first anodic peak (Fig. 5a).

The activating and inhibiting effect of 8-quinolinol applies to the same regions of the curve as with benzotriazole and aminoacridine, but is less pronounced (Fig. 5b). It accelerates the dissolution 1.5–2.0 fold in the case of oxide passivation, smoothes the curve in the case of salt passivation, and decreases  $E_{ap,1}$  by 50 mV and  $E_{ap,2}$  by 150 mV.

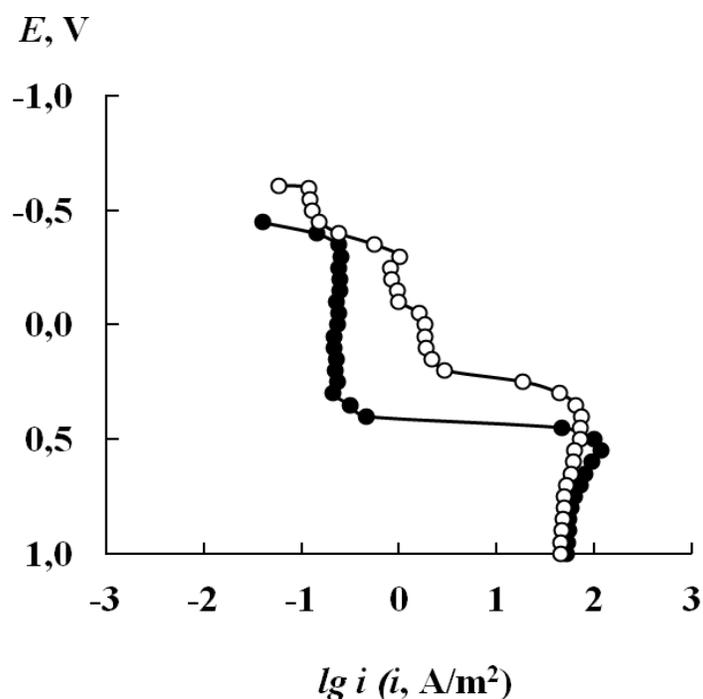
Unlike these additives, sodium phenylanthranilate, which is an adsorption-type passivator [5], performs this function even below  $E_{cor}$ . It suppresses the formation of oxides and basic salts, essentially inhibits the dissolution almost at all potentials, and increases  $E_{a,3}$  (Fig. 6).

## Conclusion

Thus, for efficient protection of bismuth in sodium chloride solution in a wide range of potentials, it is reasonable to use organic additives that favor phase passivation (oleate) or provide adsorption-type passivity (phenylanthranilate). The additives that form complexes with bismuth cations (8-quinolinol, 1,2,3-benzotriazole, and 9-aminoacridine hydrochloride) are poorer inhibitors that stimulate dissolution at some potentials.



**Figure 5.** Forward anodic polarization curves in pure 0,1 M NaCl solution (o) and with additives (●):9-aminoacridine hydrochloride (a) and 8-quinolinol (b) at  $C=5$  mmol/l.



**Figure 6.** Forward anodic polarization curves in pure 0.1 M NaCl solution (o) and in the presence of sodium phenylanthranilate at  $C=20$  mmol/l (●).

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