ON THE ANODIC DISSOLUTION OF IRON
IN NON-AQUEOUS ACETIC ACID SOLUTIONS

L.Kiss, L.DoNgoc and M.L.Varsányi

Department of Physical Chemistry and Radiology,
Eötvös Loránd University, Budapest, Hungary

The anodic dissolution of active iron has been studied by galvanostatic method in solutions of $HClO_4$, $NaClO_4$, CH_3COONa, CH_3COOLi, $LiCl$ in pure acetic acid and in acetic acid containing water in low concentrations. The dissolution rate rises with increasing acetate ion concentration and is practically independent of the presence of other ions. The reaction is of first order with respect to the acetate ion.

The passivation of iron has been studied by the potentiostatic method in solutions of CH_3COONa, $HClO_4$ in pure acetic acid and in acetic acid–water mixtures. In solutions of CH_3COONa anodic passivation occurs only in the presence of water; in solutions of $HClO_4$ it can only be observed in the absence of water. These differences are in terms of the different characteristics of the ion pairs formed in the solutions.

While investigating anodic dissolution of iron, it has been unambiguously established that when the metal is not passivated then the rate of dissolution (provided that the electrode potential is constant) increases with increasing pH[1,2], that is the hydroxide ion catalyses the anodic dissolution of iron[3,4]. Since the concentration of OH^--ions is rather low in acidified solution; it has been assumed[5], that owing to dissociation of the water, the concentration of OH^--ions must be considerably higher on the metal surface, than in the interior of the solution. This surface concentration is depending on the pH value of the solution, and on the electrode potential. Accordingly, the equations describing the mechanism of anodic dissolution comprise always a hydroxide ion *i.e.* a hydroxide-ion group (see *e.g.*[2,6-14], and the reaction order with respect to hydroxide ions of this process is greater than zero[2]. Similarly, other components of the aqueous electrolyte solution, the concentration of the neutral salt, the water activity[14,15], and particularly nature and concentration of other anions involved in the solution may interfere strongly with the rate of the anodic dissolution of iron[2,3,8,16-18]. The composition of the solution influences considerably also the passivation and activation of iron[17-19].

Among the anions, beside the hydroxide ions first of all the effect exerted by halogenide ions was investigated[2,16-18,20-25]. Under certain conditions these ions may accelerate (in passive state) or slow down (in acidified or neutral solutions) the rate of the anodic dissolution of iron[2,3,26]. Experimental data are available according to which the Cl^--ions do not interfere with the anodic dissolution[23]. The adsorption of other ions *i.e.* that of molecules may influence similarly the rate

of the process[8,9,15,26]. The effect exerted by anions is interpreted generally by the circumstance that they displace a part of the ions which were originally adsorbed on the surface[2,8,18,27]. When the newly adsorbed ion is a poorer catalyst the rate of the process decreases, in the opposite case it increases. Beside the composition of the solution, the structure of metal[11‑13], as well as the conditions prevailing on the surface[8] interfere strongly with mechanism of the anodic dissolution of pure iron.

As pointed out by several of authors[21,28‑34], the water plays an important role in the passivation of metals which was justified by experimental investigations on non-aqueous solvents[21,31‑34] In said works, it was ascertained by means of potentiostatic curves that with solutions made with non-aqueous solvents no passivation occurred. As already mentione, the supervention of passivation and its progress depend considerably on the anions being present in the solution[21,23,29,35], as well as on the deformation within the metal[36].

A uniform conception interpreting in a satisfactory manner the effect exerted by the anions (and OH^--ions) is not yet available[37]. In our opinion, the revealing of the principles regarding anodic dissolution and passivation can be furthered if the experiments are extended to non-aqueous solvents which do not contain OH^--ions. Therefore we used in experiments described in this paper acetic acid as solvent. It is a suitable solvent also because it can be easily purified and dehydrated[38,39]. In spite of the fact that relative to water its dielectric constant is small (6·29 at 19°C), it dissolves fairly well a part of salts and acids, and the conductivity of the solution thus formed is generally great enough to permit electrochemical measurements.

Relatively few data are available as regards ionization and neutralization of metals in acetic acid[39‑41]. According to literature data, some authors endeavoured to establish the charge number of the metal ions turned into solution by the extent of the anodic dissolution[39,40]. It has been established that the passage of iron into solution results in divalent ions. As suggested by Heitz[41] in non-aqueous acetic acid solution the iron dissolves according to an electrochemical mechanism.

EXPERIMENTAL

The equipment used for recording stationary galvanostatic as well as stationary potentiostatic curves was described in our previous publication[42]. The electrode potential was determined by means of a precision pH-titrimeter, type Radelkisz OP 205, the potentiostatic measurements were carried out by a potentiostat PB 410.

The galvanostatic measurements were carried out by a calomel electrode containing 0·3M-$NaClO_4$ prepared from non-aqueous glacial acetic acid saturated with NaCl[43], the potentiostatic measurements again by a calomel electrode saturated with water. The electrode potentials mentioned in this paper refer to the said reference electrodes.

The electrodes under investigations were made of iron containing 99·9% of iron, brand Puron. The acetic acid used for preparing the solution was previously dehydrated in the manner described in the literature. Water content of the solutions was checked by the Fischer titration method. The experiments followed under nitrogen atmosphere, at room temperature. At the current densities applied in the case of galvanostatic measurements, the ohmic potential drop between the end of the Luggin capillary and the iron electrode was negligible.

In order to check that under the conditions of our galvanostatic investigations solely the anodic dissolution of iron occurs, the efficiency of the anodic dissolution was studied. Measuring then the loss of weight of the anode and the charge passing through the electrode it has been established that the measured dissolved amount was always greater than the calculated one (assuming two positive charges for iron).

The actual number of charges of the iron turned into solution (according to nine measurements) yielded $1 \cdot 81 \pm 0 \cdot 09$ (see[40]). This fact led to the conclusion that in the solution and over the current density interval under investigation, solely the dissolution of iron takes place.

The relationship between the electrode potential (φ) and the current density (i) was measured mainly in the solutions compiled in Table I. Figures $1-3$ present some polarization curves determined by stationary galvanostatic method in solutions of different composition. It is evident that under the conditions used the iron undergoes no passivation. The anodic dissolution of the iron surface is uniform. At great current densities the curves φ *vs* log i exhibits a linear section. For the anodic curve the average b for the Tafel-slope — as shown in Table I — yielded 62 ± 3 mV. On this basis the value of b can be considered as 60 mV.

The linear section of the curves can be described by the following relation:

$$i = k'' \exp\left(\varphi/b'\right), \tag{1}$$

where $b' = 0 \cdot 43b$, k'' is a constant depending on composition of the solutions and on potential of the reference electrode.

Figs $1-3$ demonstrate that the rate of anodic dissolution increases with decreasing "acidity" of the solutions at identical potentials. As known the acetic acid
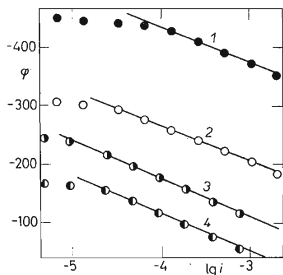

FIG. 1

Galvanostatic Polarization Curves of the Solutions in Non-Aqueous Acetic Acid

1 $0 \cdot 5$M-CH$_3$COOONa, *2* $0 \cdot 17$M-NaClO$_4$, *3* $0 \cdot 2$M-NaClO$_4$ + $0 \cdot 05$M-HClO$_4$, *4* $0 \cdot 2$M-NaClO$_4$ + $0 \cdot 065$M-HClO$_4$; φ in mV, i in A/cm^2.
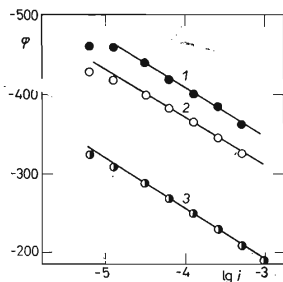
FIG. 2

Galvanostatic Polarization Curves for the Solutions in Non-Aqueous Acetic Acid

1 $0 \cdot 5$M-CH$_3$COOLi, *2* $0 \cdot 5$M-CH$_3$COOLi + $0 \cdot 5$M-LiCl; *3* $0 \cdot 5$M-LiCl; φ in mV, i in A/cm^2.

dissociates similarly to water:

$$2\,CH_3COOH \;\rightleftarrows\; CH_3COOH_2^+ + CH_3COO^-. \qquad (A)$$
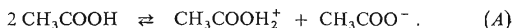
The ionic product is

$$K = \left[AcH_2^+\right]\left[Ac^-\right], \qquad (2)$$

where $\left[AcH_2^+\right]$ stands for concentration (activity) of the $CH_3COOH_2^+$, and $\left[Ac^-\right]$ for that of the CH_3COO^--ions. According to several authors see[38], the value of K lies between 10^{-13} and 10^{-15}. Thus, in acetic acid medium the rate of anodic dissolution of iron increases with increasing concentration of the acetic anion, similarly as in aqueous medium with concentration of the OH^--ions. Consequently, the relation (1) can be written as

$$i = k'\left[Ac^-\right]^v \exp\left(\varphi/b'\right), \qquad (3)$$

where v is the reaction order with respect to be acetic ion, while k' is a constant.

In order to check the equation (3) we prepared the equilibrium hydrogen electrode with acetic acid solution[44] the potential of which (in the case of a constant hydrogen gas pressure) follows the relation

$$\varphi(H_2) = \varphi' + (RT/F)\ln\left[AcH_2^+\right]. \qquad (4)$$

TABLE I
Potentials and Current Densities of Iron Electrode in Solutions in Acetic Acid

Solution	$\varphi(H_2)$ mV	φ, mV[a]	φ_{st} mV	b mV	$t_{st} \cdot 10^6$ A/cm^2	Number of measurements
0·5м-CH$_3$COONa	−560	−410	−460	60	40	17
0·17м-NaClO$_4$	−230	−240	−310	58	16	11
0·2м-HClO$_4$	+137	+ 30	− 50	59	15	8
0·2м-HClO$_4$ + 0·31м-H$_2$O	+ 92	− 3	− 85	64	15	2
0·2м-HClO$_4$ + 0·62м-H$_2$O	+ 66	− 18	−120	68	8	3
0·5м-CH$_3$COOLi	−340	−390	−460	62	12	3
0·5м-LiCl	−170	−230	−340	62	6	2
0·5м-LiCl + 0·5м-CH$_3$COOLi	−290	−340	−440	60	8	4
0·25м-CH$_3$COONa + 0·15м-NaClO$_4$	−320	−350	−440	59	10	13
0·5м-CH$_3$COOLi + 0·1м-LiCl	−330	−340	−450	59	5	2
0·2м-NaClO$_4$ + 0·05м-HClO$_4$	− 90	−144	−250	66	6	1
0·2м-NaClO$_4$ + 0·065м-HClO$_4$	− 35	− 97	−175	63	12	1

[a] For $i = 250$ mA/cm^2.

Here φ' is a constant the value of which is depending both on the reference electrode and the hydrogen pressure. According to equation (2) it can be written that

$$\varphi(H_2) = \varphi'' + (RT/F) \ln [Ac^-], \tag{5}$$

where $\varphi'' = \varphi' + (RT/F) \ln K$. Derivating from equation (5) the value of $[Ac^-]$ and substituting it in equation (3) we get

$$i = k \exp [- vF\varphi(H_2)/RT] \exp (\varphi/b), \tag{6}$$

where $k = k' \exp (vF\varphi''/RT)$. By rearranging Eq. (6) and evaluating the constants for 25°C we obtain

$$\varphi = b \log k + (vb/59) \varphi(H_2) + b \log i. \tag{7}$$

By means of equation (7) the correctness of equation (3) can be checked, and the reaction order can be evaluated. For 250 μA/cm² and for solutions of different composition $(cf.$ Table I) we obtained a $\varphi - \varphi(H_2)$ plot which can be approximated by a straight line of the slope 0·90; since $b \approx 60$ mV is $v \approx 1$.

A small amount of water (1 mol per 1 l of solution) added to a solution containing sodium acetate did not alter the rate of the anodic process within the experimental
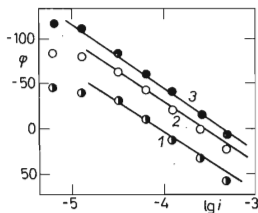
FIG. 3

Galvanostatic Polarization Curves for the Solutions in Acetic Acid Containing Water

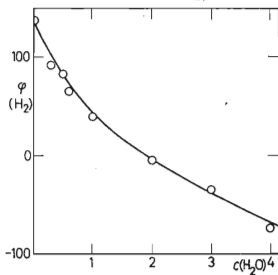*1* 0·2M-HClO₄, *2* 0·2M-HClO₄ + 0·31M-H₂O, *3* 0·2M-HClO₄ + 0·62M-H₂O; φ in mV, i in A/cm².

FIG. 4

Dependence of the Hydrogen Electrode Potential on the Change in the Concentration of Water

0·2M-HClO₄ in acetic acid, $\varphi(H_2)$ in mV, $c(H_2O)$ in mol/l.

errors. Nevertheless (Fig. 3) the water (0·3 mol/l resp. 0·6 mol/l) added to 0·2M-$HClO_4$ altered considerably the rate of the anodic process. On the effect of water, the rate of anodic dissolution of iron increased considerably, and accordingly, the anodic polarization curve shifted towards the negative potentials.

This phenomenon can be interpreted by the circumstance, that the proton is more strongly bonded by water than by acetic acid and thus in the presence of water, the following process (leading to equilibrium) occurs:

$$CH_3COOH_2^+ + H_2O \rightarrow CH_3COOH + H_3O^+ \qquad (B)$$
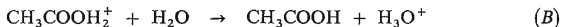
Consequently, the equilibrium of the process (A) is shifted towards the upper arrow, that is the concentration of the acetate ions in the solution increases, and the solution becomes more and more "alkaline". Accordingly, if water is added to the 0·2M-$HClO_4$ solution, the equilibrium hydrogen electrode potential of the solution (Fig. 4) is shifted with increasing water concentration towards a negative direction. The linearity of the $\varphi - \varphi(H_2)$ plot (including solutions containing water) show that the rate of the anodic dissolution of iron — independently of the ions involved in the solution — is determined predominantly by concentration of the acetate ions, the effect of other components being within the experimental errors. The promoting effect that the acetate ions exert on anodic dissolution of iron could be observed also with measuring on non-aqueous formamide solution.

All these experimental data seems to indicate that in acetic acid medium, the acetate ions plays the same role as the OH^--ion in aqueous solution. Obviously, on the basis of the obtained kinetic parameters, the mechanism for anodic dissolution cannot be interpreted on the analogy neither of the Bockris, nor of the Heusler mechanism[11]. In the former case, namely, the values $b = 40$ mV and $v = 1$, and in the latter case the values $b = 30$ mV and $v = 2$ should be obtained.

On the other hand, our experimental results are in agreement with the data obtained by Lorenz and coworkers[27] for the anodic dissolution of iron in the aqueous solution of hydrochloric acid (pH $< 1·5-2$). However, in the case of concentrated acetic acid also the adsorption of acetate ions on the surface must be taken into account, since the data obtained for rate of the spontaneous dissolution leads to the conclusion that the acetate ion must interfere also with the process of hydrogen discharge.

Our experimental data coincide with the following mechanism for the anodic dissolution of iron:

$$2\ AcH \rightleftarrows AcH_2^+ + Ac^- , \qquad (C)$$

$$Fe + Ac^- \rightarrow FeAc^+ + 2\ e . \qquad (D)$$
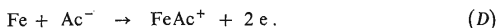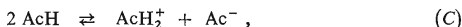
Process (C) is a quick step leading to equilibrium, whereas process (D) a slow, rate

determining one. Accordingly, the relation describing rate of the anodic dissolution can be written as

$$i = k[\text{Ac}^-] \exp\left(2\alpha F\varphi/RT\right), \qquad (8)$$

where k is a constant depending on the reference electrode, α is the charge transfer coefficient.

The passivation of iron was investigated by the potentiostatic method in aqueous and non-aqueous acetic acid solutions containing mainly sodium acetate and perchloric acid. The potential was usually altered in steps of 50, respectively of 100 mV, then upon a waiting time of 3 min, the value of the current passing through the electrode was read. After the elapse of this time, the intensity of the current passing through the electrode exhibited generally no change.

In Fig. 5 the potentiostatic curves $\varphi - \lg i$ are presented which were determined on an iron electrode in water–acetic acid mixture containing 0·5M sodium acetate. As it can be seen — with exception of the non-aqueous acetic acid solution — the passivation of the iron electrode takes place in each case. Over the passive range, the rate of dissolution increases with increasing acetic acid content of the solution. With potentials which are positive enough, the rate of active anodic dissolution
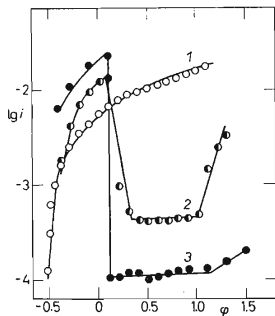

Fig. 5

Potentiostatic Polarization Curves of 0·5M-CH$_3$COONa

Solvent: *1* non-aqueous CH$_3$COOH, *2* 90% CH$_3$COOH + 10% H$_2$O, *3* 50% CH$_3$COOH + 50% H$_2$O; i in A/cm^2, φ in V.
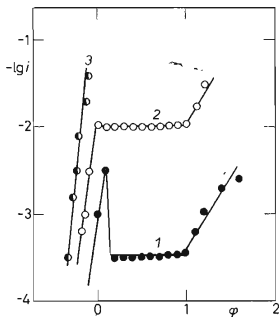
Fig. 6

Potentiostatic Polarization Curves of 0·5M-HClO$_4$

Solvent: *1* non-aqueous CH$_3$COOH, *2* 98% CH$_3$COOH + 2% H$_2$O, *3* 90% CH$_3$COOH + 10% H$_2$O; i in A/cm^2, φ in V.

increases with the water content. The altering of the sodium acetate concentration over the range from 0·1 to 0·5 mol/l yields potentiostatic polarization curves of similar shape.

The experimental data allow the statement, that in an acetic acid solution containing sodium acetate, the passivation of iron occurs only in the presence of water, which is otherwise in good agreement with the data reported by other authors who experimented with non-aqueous solutions[21,31−34].

For non-aqueous and aqueous acetic acid solutions containing 0·5M-HClO₄, the potentiostatic curve for iron is shown in Fig. 6. Apparently, in non-aqueous solutions the shape of the potentiostatic curve is indicative of a passivation, in contrary to the literature data referring to non-aqueous solvents as well as to the data obtained for sodium acetate solution. On the other hand, on addition of water the passivation disappears and the iron cannot be passivated. In accordance with the data shown in Fig. 3, at a stage corresponding to the active dissolution of iron, the rate of anodic dissolution increases with the increasing water concentration in this case, too. The altering of the perchlorate concentration from 0·1 to 0·5 mol yields a potentiostatic polarization curve of similar shape.

In order to reveal the behavior of the iron electrode in solution containing sodium acetate and perchloric acid, respectively, the effect of the stirring of electrolytes on the polarization curve was investigated by the rotating disk electrode method (Fig. 7) in sodium acetate solutions the revolution number of the electrode practically does not affect the character of potentiostatic curves. In perchloric acid solutions, the shape
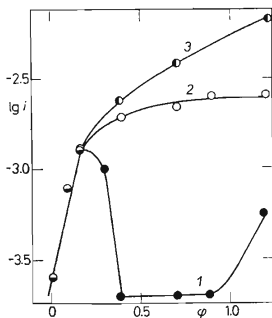
Fig. 7

The Effect of Revolution Number of the Electrode on the Shape of the Potentiostatic Curves
0·2M-HClO₄ in non-aqueous CH₃COOH. Revolution number of the rotating disk electrode: *1* 0, *2* 230, *3* 1 320 min⁻¹, φ in V, *i* in A/cm².

of the potentiostatic curves do not change in the active region with revolution number of the electrode, but in the passive region the current intensity increases considerably and with the shift of the potential in the positive direction, the current density drop characteristic of passivation does not occur. In the case of CH_3COONa-solution the passivation occurring in addition of water is probably due to the oxide layer formed on the iron surface, the dissolution of which is independent of hydrodynamic conditions. In the case of the nonaqueous solutions of $HClO_4$ again, the passivation must be attributed to the accumulation and slow displacement of the dissolution product on the surface, that is to the solubility promoting component, *e.g.* to the acetate ions penetrating to the surface. This is similar to the dissolution of iron in aqueous NaCl solution at great current densities, where the occurring of passivation is determined likewise by a convective diffusion[45].

Water accelerates in each case the rate of active dissolution. This effect can be probably attributed to the circumstance, that it is adsorbed on the surface and its participation in building-up of the solvate shell promotes anodic dissolution. On the other hand, as pointed out above, with increasing concentration of water the concentration of the acetate ions increases and this results in an increasing rate of active dissolution. With solutions containing perchloric acid, at the potentials corresponding to passivation this effect is predominant, together with the effect that on addition of water the product of anodic dissolution dissolves better. The fact that the dissolution of iron(II) acetate increases considerably in the presence of water seems to justify the above statement. Thus, in nonaqueous acetic acid the solubility of iron(II) acetate in the presence of $0.5M$-$HClO_4$ was 0.46 g/100 ml, while in the case of 90% acetic acid + 10% water in the presence of $0.5M$-$HClO_4$, the solubility was 3.5 g/100 ml. In sodium acetate solutions the solubility exhibits a similar increase in the presence of water.

The circumstance, that with sodium acetate and perchloric acid solutions the interaction between the water and the components involved in the solution is rather different in these two alternatives, may interfere considerably with our experimental data. In the first alternative, it can be assumed that in the solution mainly $[(CH_3COOH)_2Na^+CH_3COO^-]$ complexes (ion pairs) are formed. Actually, the addition of water to the solution does not decompose the complex. Prior to addition of water in perchloric acid solution $[(CH_3COOH)_2H^+ClO_4^-]$ complexes are present, in which owing to the effect of water addition (since the proton is bonded more strongly to water) the following process takes place

$$[(CH_3COOH)_2H^+ClO_4^-] + H_2O \ \rightleftarrows \ (CH_3COOH)_2 + [H_3O^+ClO_4^-].$$

$$(E)$$
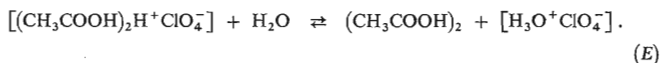
In this case the ion pair contains hydroxonium ion and the iron passivity is impeded by them. In solutions containing sodium acetate, on the other hand, at a certain

potential the water adsorbed on the surface enables the formation of a protective layer that is independent of hydrodynamic conditions.

It can be said, that in accordance with the suggestions of Heitz[41], the anodic dissolution of iron follows an electrochemical mechanism. However, on the basis of our experimental results, we cannot accept the statement of the said author, that the passivation observed with carbonic acids is generally due to the $Me(Carb)_n$ protective layer. The experimental data seem to justify our opinion that in sodium acetate solutions the passivation occurs only in the presence of water.

REFERENCES

1. Kabanov B. N., Burstein R. Ch., Frumkin A. N.: Discussions Faraday Soc. *1*, 259 (1947).
2. Florianovič G. M., Sokolova L. A.: Kolotyrkin J. M.: Elektrochimija *3*, 1027 (1967); *3*, 1359 (1967).
3. Kabanov B. N.: *Elektrochimija Metallov i Adsorbcija*, p. 140. Izd. Nauka, Moscow 1966.
4. Sedzimir J., Zembura Z., Ziolkowska W.: Werkstoffe u. Korrosion *17*, 556 (1966).
5. Bonhoeffer K. F., Heusler K. F.: Z. Elektrochem. *61*, 122 (1957).
6. Heusler K. E.: Z. Elektrochem. *62*, 582 (1958).
7. Hurlen T.: Electrochim. Acta *7*, 653 (1962).
8. Bockris J.O'M., Drazic D., Despic A.: Electrochim. Acta *4*, 325 (1961).
9. Kelly E. J.: J. Electrochem. Soc. *112*, 124 (1965); *115*, 111 (1968).
10. Zinter J. D., Rotinjan A. L.: Elektrochimija *2*, 1371 (1968).
11. Lorenz W. J., Eichkorn G.: Ber. Bunsenges. Phys. Chem. *70*, 99 (1966).
12. Eichkorn G., Lorenz W. J.: Metalloberfläche *22*, 102 (1968).
13. Eichkorn G., Lorenz W. J., Albert L., Fischer H.: Electrochim. Acta *13*, 183 (1968).
14. Voigt C.: Electrochim. Acta *13*, 2037 (1968).
15. Schwabe K., Voigt C.: Werkstoffe u. Korrosion *16*, 125 (1965).
16. Iofa Z. A., Medvedeva L. A.: Dokl. Akad. Nauk SSSR *69*, 213 (1949).
17. Iofa Z. A., Roždestvenskaja G. B.: Dokl. Akad. Nauk SSSR *91*, 1159 (1953).
18. Heusler K. E., Cartledge G. H.: J. Electrochem. Soc. *108*, 732 (1961).
19. Kolotyrkin J. M.: Uspechi Chimii *31*, 3 (1962).
20. Schwabe K., Voigt C.: Electrochim. Acta *14*, 853 (1969).
21. Frejman L. I., Kolotyrkin J. M.: Zaščita Metallov *5*, 139 (1969).
22. Golovina G. V., Florianovič G. M., Kolotyrkin J. M.: Elektrochimija *1*, 12 (1965).
23. Nobe K., Tobias R. F.: Corrosion *20*, 262 (1964).
24. Arvia A. J., Podesta J. J.: Corrosion Sci. *8*, 203 (1968).
25. Cafferty E. Mc., Zettlemeyer A. C.: J. Phys. Chem. *71*, 2444 (1967).
26. Frejman L. I., Kolotyrkin J. M.: Dokl. Akad. Nauk SSSR *171*, 1138 (1966).
27. Lorenz W. J., Yamaoka H., Fischer H.: Ber. Bunsenges. Phys. Chem. *67*, 932 (1963).
28. Schwabe K.: Werkstoffe u. Korrosion *18*, 961 (1967).
29. Kolotyrkin J. M.: Zaščita Metallov *3*, 131 (1967).
30. Hoar T. P.: Corrosion Sci. *7*, 341 (1967).
31. Kolotyrkin J. M., Kossyj G. G.: Zaščita Metallov *1*, 271 (1965).
32. Šmidt V.: Zaščita Metallov *5*, 608 (1969).
33. Cinman A. I., Kartevič A. N.: Zaščita Metallov *5*, 517 (1969).
34. Schwabe K., Schmidt W.: Corrosion Sci. *10*, 143 (1970).
35. Frejman L. I., Kolotyrkin J. M.: Zaščita Metallov *1*, 161 (1965); Dokl. Akad. Nauk SSSR *162*, 376 (1965).

36. Frejman L. I., Kolotyrkin J. M., Givental A. J.: Zaščita Metallov *1*, 286 (1965).
37. Erdey-Grúz T.: *Elektródfolyamatok kinetikája*, p. 289. Akadémiai Kiadó, Budapest 1969.
38. Jander G., Spandau H., Addison C. C.: *Chemie in Niederen Fettsauren und Ihren Derivaten.* Akademie Verlag, Berlin.
39. Odrit L., Klejnberg J.: *Nevodnyje Rastvoriteli.* Izd. Inostr. Lit., Moscow 1965.
40. Brouillet P., Epelboin J., Froment M.: Compt. Rend. *239*. 1795 (1954).
41. Heitz E.: Ber. Bunsenges. *73*, 1085 (1969); Werkstoffe u. Korrosion *21*, 360 (1970).
42. Kiss L.: Magy Kem. Folyoirat *69*, 507 (1963); Kiss L., Körösi A., Farkas J.: Ann. Univ. Sci. Budapest, Sect. Chim. *9*, 3 (1967).
43. Ives D. J. G., Janz G. J.: *Reference Electrodes*, p. 449. Academic Press, New York 1961.
44. Bockris J. O'M.: Discussion Faraday Soc. *1*, 95 (1947).
45. Davidov A. D., Kaščejev V. D., Kabanov B. N.: Elektrochimija *5*, 221 (1969).