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INVESTIGATION OF THE SURFACE PROPERTIES OF PLATINUM, RHODIUM AND IRIDIUM ELECTRODES IN HYDROFLUORIC ACID SOLUTIONS

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The surface properties of Pt, Rh and Ir electrodes in solutions containing fluoride anions have not been studied as thoroughly as those in solutions containing other anions. The literature data for Pt are scanty and rather contradictory[1–5]. Some problems of the technique of measurements in HF solutions have been discussed in ref. 6 and lower adsorption of fluoride anions, as compared with sulfate anions, on Pt and Rh electrodes was assumed on the basis of the potentiodynamic curves. The surface properties of the Ir electrode in HF solutions have not been studied at all. This paper contains the results of a systematic study of the surface properties of Pt, Rh and Ir electrodes in solutions of HF and of acidified fluorides. To obtain quantitative data, the methods developed on the basis of the thermodynamic theory of the platinum hydrogen electrode were used (see, *e.g.* refs. 7–12).

Sulfate and perchlorate anions were found to be the least specifically adsorbed at platinum metals of the anions studied earlier. However, according to ref. 13, at Pt and Rh the ClO_4^- anions are reduced to chloride anions to an appreciable degree. For this reason, our results for fluoride anions were compared with the respective data for sulfuric acid and acidified sulfates.

EXPERIMENTAL

The measurements were carried out in a cell made from Teflon and trifluoropolyethylene (Fig. 1). It consisted of the compartments of the operating electrode (1), the reference electrode (2) and the auxiliary electrode (3), as well as of two vessels (4 and 5) for replacing the solutions, in which the operating and reference electrodes were placed. Platinum gauzes (6) covered with electrodeposited Pt, Rh and Ir layers were used as operating electrodes. The auxiliary electrode was a Pt wire (7) and the reference electrode a Pt tube (8), platinized from the bottom end[6]. The compartments of the electrodes were separated from one another by Teflon stopcocks (9). At closed stopcock, the resistance in the circuit operating electrode–auxiliary electrode in 1 *M* HF was *ca.* 100 kΩ. There were two stopcocks between the compartments 1 and 2 to ensure that hydrogen did not reach the operating electrode. The solutions to be replaced were removed through the openings in the cell bottom closed by Teflon stopcocks (10). The important requirement for the cell—its tightness was ensured by the use of conical elements for connecting various parts of the cell (see, *e.g.* Fig. 1, element b).

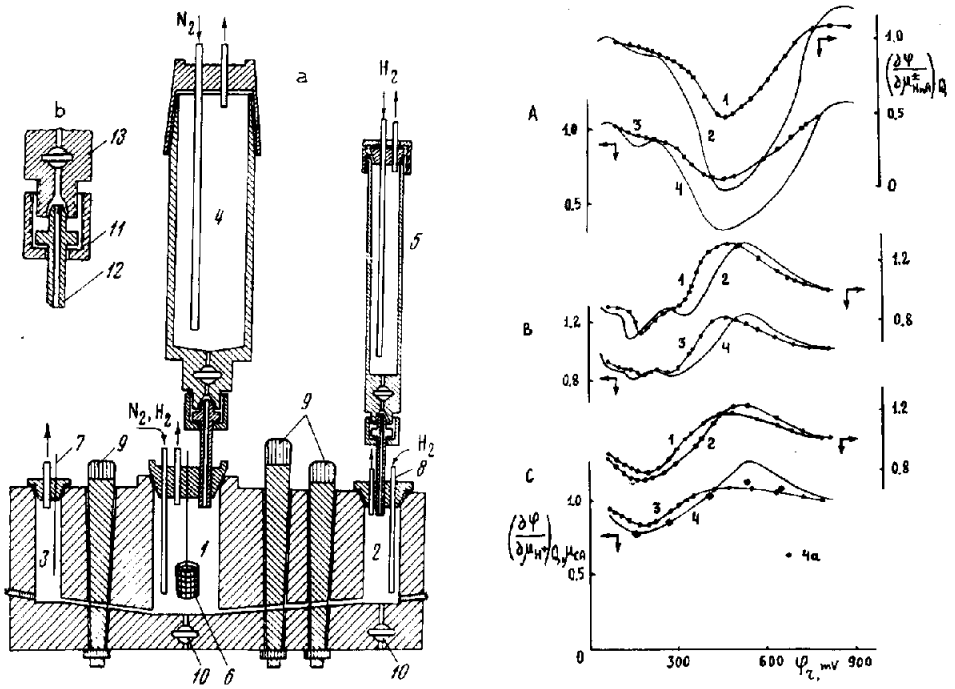


Fig. 1. (a) Teflon cell for measurements in hydrofluoric acid solutions (for details, see text); (b) Vessels for replacement of solutions at compartments 1 and 2. (11), Teflon washer; (12), adjustable conical element; (13), bottom part of vessel for replacement of solutions.

Fig. 2. Curves of the isoelectric potential shifts of (A) Pt, (B) Rh and (C) Ir electrodes in solutions: (1) 0.14 *M* HF; (2) 0.005 *M* H_2SO_4 (A and B according to the data of refs. 25 and 26); (3) 0.3 *M* HF + 0.12 *M* KF; (4) 0.005 *M* H_2SO_4 + 0.05 *M* Na_2SO_4 (according to the data of refs. 32–35).

The measurements of the isoelectric potential shifts and of the charging curves were carried out on the same electrodes with geometric surface area 30 cm^2 (Pt), 14 cm^2 (Rh) and 18 cm^2 (Ir). The true surface areas of these electrodes were: 2.4 m^2 (Pt), 1.1 m^2 (Rh) and 1.2 m^2 (Ir). The potentiodynamic curves were measured on smaller electrodes with the values of true surface area equal to 0.5 m^2 (Pt), 0.25 m^2 (Rh) and 0.5 m^2 (Ir). The true surface areas of the electrodes were determined from the length of the hydrogen section of the charging curves assuming the amount of hydrogen adsorbed at the reversible hydrogen potential in 0.5 *M* H_2SO_4 in the case of Pt 210 $\mu C\ cm^{-2}$ (ref. 14) of Rh and Ir 220 $\mu C\ cm^{-2}$ (refs. 15 and 16). Platinization was carried out from a 2% H_2PtCl_6 solution for 3 h at the current density $i = 2$ mA cm^{-2}, which ensured a sufficiently positive deposition potential[17]. Rhodium plating was performed from a 2% $RhCl_3$ + 1.5 *M* HCl solution at $i = 6$ mA cm^{-2} and continued for 2 h (ref. 18), iridium plating from a 2% Na_2IrCl_6 + 0.1 *M* HCl solution at $\varphi_r = +100$ mV and $t^0 = 60°C$ for 20 h (ref. 19).

HF of the "special purity" grade was subjected to additional purification by cathodic polarization for a week on a large Pt/Pt gauze[6], which periodically was subjected to anodic–cathodic polarization in H_2SO_4, whereupon it was carefully washed with twice-distilled water. KF of "analytically pure" grade was twice

recrystallized from twice-distilled water in a Teflon vessel and calcined in a Pt cup at 600°C. The experiments were carried out at 20±1°C.

RESULTS AND DISCUSSION

(1). The adsorption properties of Pt, Rh and Ir electrodes in HF and HF+KF solutions

The adsorption properties of the Pt, Rh and Ir electrodes were studied by the method of the isoelectric potential shifts coupled with the measurement of charging curves[20–22]. According to the thermodynamic theory of the platinum hydrogen electrode, the following relations are valid for HF and HF+KF solutions[7–10,12]:

$$\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu^{\pm}_{HF}} = -\frac{1}{2}\left(\frac{\partial \varphi_r}{\partial \mu^{\pm}_{HF}}\right)_Q \left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu^{\pm}_{HF}} = -\frac{1}{2}\left[\left(\frac{\partial \varphi}{\partial \mu^{\pm}_{HF}}\right)_Q - 1\right]\left(\frac{\partial Q}{\partial \varphi}\right)_{\mu^{\pm}_{HF}} \quad (1)$$

$$\left(\frac{\partial \Gamma_{H^+}}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_{KF}} = -\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}}\right)_{Q,\mu_{KF}}\left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{H^+},\mu_{KF}} =$$

$$= -\left[\left(\frac{\partial \varphi}{\partial \mu_{H^+}}\right)_{Q,\mu_{KF}} - 1\right]\left(\frac{\partial Q}{\partial \varphi}\right)_{\mu_{H^+},\mu_{KF}} \quad (2)$$

where Γ_{H^+} is the Gibbs adsorption of H^+ ions, μ_{H^+}, $\mu^{\pm}_{HF}$, μ_{KF} are the respective chemical potentials, Q the total surface charge ($Q=-\Gamma_H$)*, φ the electrode potential, φ_r the potential referred to the reversible hydrogen electrode in the same solution ($\varphi_r=\varphi-\mu_{H^+}$). All the quantities in eqns. (1) and (2) are expressed in electric units. The adsorption was calculated per 1 cm^2 of true surface.

The values of the derivatives $(\partial\varphi/\partial\mu^{\pm}_{HF})_Q$ and $(\partial\varphi/\partial\mu_{H^+})_{Q,\mu_{KF}}$, determined by the isoelectric potential shifts method, are shown in Fig. 2. The isoelectric shifts were determined replacing the 0.018 *M* HF solution by 0.9 *M* HF and 0.15 *M* HF+0.12 *M* KF by 1.5 *M* HF+0.12 *M* KF and referred to a solution with a medium pH value (0.14 *M* HF, pH=2.0 and 0.3 *M* HF+0.12 *M* KF, pH=2.4, respectively). The value of $\Delta\mu^{\pm}_{HF}$ was calculated by means of the equation $\Delta\mu^{\pm}_{HF}=(RT/F)\Delta\log(\gamma_{\pm}c_{HF})$ from the data given in ref. 23. The value of $\Delta\mu_{H^+}$ for HF+KF solutions was determined experimentally from the change in the potential difference operating electrode – reference electrode after replacement of the solution in the compartment of the reference electrode; $\Delta\mu_{H^+}$ was 79±1 mV.

The slow charging curves were measured in solutions with medium pH values (Fig. 3). From these curves the values of the derivatives $(\partial Q/\partial\varphi_r)_{\mu^{\pm}_{HF}}$ and $(\partial Q/\partial\varphi_r)_{\mu_{H^+},\mu_{KF}}$ were determined by graphical differentiation. Then by means of eqns. (1) and (2) the derivatives $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu^{\pm}_{HF}}$ and $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+},\mu_{KF}}$ were calculated and the $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu^{\pm}_{HF}}-\varphi_r$ and $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+},\mu_{KF}}-\varphi_r$ curves were plotted, by the integration of which the dependences of Γ_{H^+} on φ_r were found (Figs. 4, 5, curves 1). The pH values of the H_2SO_4 and $H_2SO_4+Na_2SO_4$ solutions, for which the curves are also given in Figs 2–5, are close to those of 0.14 *M* HF and 0.3 *M* HF solutions.

In the integration of the $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu^{\pm}_{HF}}-\varphi_r$ curves at Pt, Rh and Ir, the

* The detailed interpretation of Q is given in ref. 11.

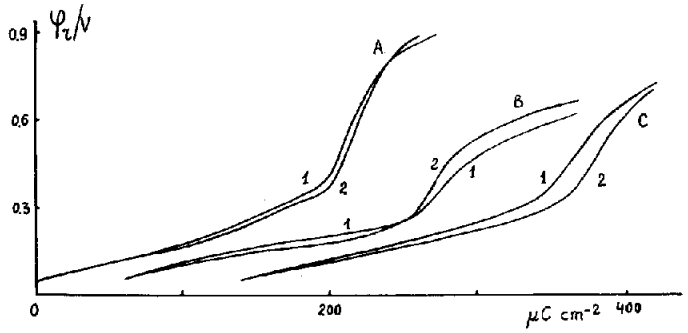


Fig. 3. Charging curves of (A) Pt, (B) Rh and (C) Ir electrodes in solutions: (1) 0.14 *M* HF; (2) 0.02 *M* H_2SO_4.

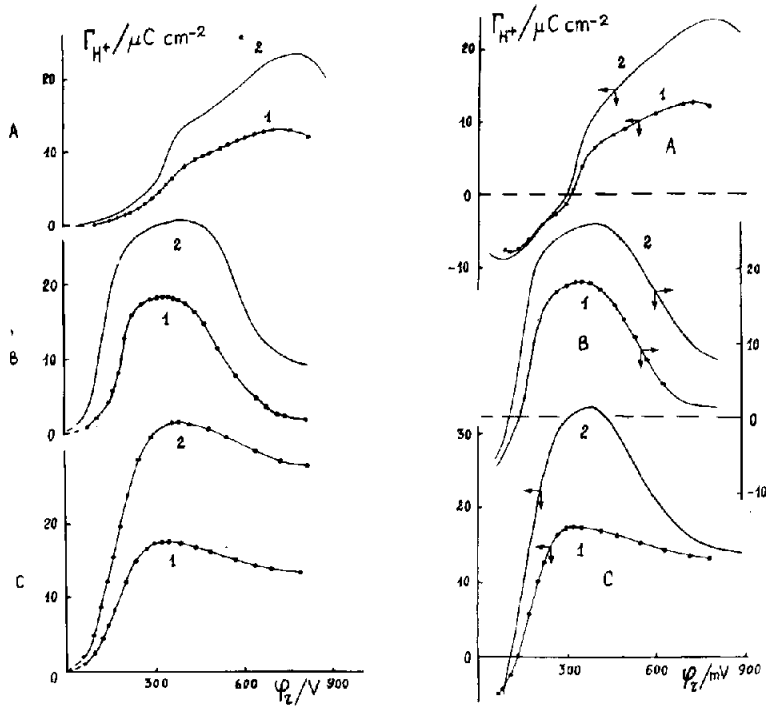


Fig. 4. Γ_{H^+} – φ_r curves at (A) Pt, (B) Rh and (C) Ir electrodes in solutions: (1) 0.1 *M* HF; (2) 0.005 *M* H_2SO_4 (A and B according to the data of refs. 25 and 26).

Fig. 5. Γ_{H^+} – φ_r curves of (A) Pt, (B) Rh and (C) Ir electrodes in solutions: (1) 0.3 *M* HF + 0.12 *M* KF; (2) 0.005 *M* H_2SO_4 + 0.5 *M* Na_2SO_4 (according to the data of refs. 32–35).

value of $\Gamma_{H^+}=0$ at $\varphi_r=0$ was taken as the integration constant, since in solutions of pure acid HA $\Gamma_{H^+}=\Gamma_{A^-}$ and, by analogy with sulfate anions, at $\varphi_r=0$ the adsorption of fluoride anions[24–26] can be taken to be zero. If in HF + CA solutions $[C^+] \gg [H^+]$, then $\Gamma_{H^+}=\varepsilon=\Gamma_{A^-}-\Gamma_{C^+}$, where ε is the surface free charge[11]. Since at φ_r values of the "double layer" region on a positively charged surface the

adsorption of alkali-metal cations in $H_2SO_4 + C_2SO_4$ solutions is insignificant[27,28], it can be assumed that in HF + KF solutions as well at φ_r values of the "double layer" region $\Gamma_{K^+} \simeq 0$. Therefore the integration constants of the $\Gamma_{H^+}-\varphi_r$ curves in HF + KF were determined from the condition that $\Gamma_{F^-}^{max} \simeq \Gamma_{H^+}^{max}$ in HF + KF is equal to $\Gamma_{F^-}^{max} = \Gamma_{H^+}^{max}$ in HF. The possible dependence of $\Gamma_{F^-}^{max}$ on the concentration of F^- ions at $[F^-] > 10^{-2}$ M was neglected. It was not possible in the case of HF and HF + KF solutions to determine the integration constants of the $\Gamma_H-\varphi_r$ curves by means of direct adsorption measurements (as was done in refs. 9, 10, 25 and 26) because even at sufficiently high pH values these solutions contain large amounts of HF owing to the low dissociation constant of hydrofluoric acid.

It is clear from Fig. 2 that the minimal values of $(\partial\varphi/\partial\mu_{HA}^{\pm})_Q$ and $(\partial\varphi/\partial\mu_{H^+})_{Q,\mu_{CA}}$ in HF and HF + KF solutions are higher than in H_2SO_4 and $H_2SO_4 + Na_2SO_4$. These results show that the surface coverage of Pt, Rh and Ir electrodes with adsorbed hydrogen and oxygen atoms at these φ_r in solutions with fluoride anions is greater than in solutions with sulfate anions. At Pt, Rh and Ir the isoelectric potential shifts on the ascending branches of the curves in HF and HF + KF solutions reach values larger than (or equal to) 1 at less positive φ_r than in H_2SO_4 and $H_2SO_4 + Na_2SO_4$. This is evidently due to an earlier displacement of the fluoride anions by adsorbed oxygen, as compared to sulfate anions. The shape of the charging curves in HF and H_2SO_4 also points to an earlier oxygen adsorption in HF solutions (Fig. 3). From what has been said above, it can be already assumed that at Pt, Rh and Ir fluoride anions are less strongly adsorbed than sulfate anions.

Curves 1 in Fig. 4 characterize quantitatively the dependence of the adsorption of fluoride anions on φ_r at Pt, Rh and Ir. It is clear from Fig. 4 that the adsorbability of fluoride anions at Pt, Rh and Ir over the whole range of φ_r (50–800 mV) is markedly less than for sulfate anions (Fig. 4, curves 2). The maximum values of Γ_{A^-} (in $\mu C\ cm^{-2}$) are: $\Gamma_{F^-}^{max} = 12.5$ (Pt), 18 (Rh), 17 (Ir) whereas $\Gamma_{SO_4^{2-}}^{max} = 23$ (Pt), 28 (Rh), 33 (Ir). The decrease in the amounts of adsorbed fluoride and sulfate anions after a certain φ_r value is due to their displacement by adsorbed oxygen. Since fluoride anions are more weakly adsorbed, their displacement starts earlier and the values of $\Gamma_{F^-}^{max}$ correspond to less positive φ_r than $\Gamma_{SO_4^{2-}}^{max}$ values. It should be pointed out that the solutions being investigated along with the F^- and SO_4^{2-} ions, contain considerable amounts of HF_2^- and HSO_4^- ions, and therefore the characteristics given here represent certain averages for F^- and HF_2^- and SO_4^{2-} and HSO_4^- as well.

The comparison of the $\Gamma_{H^+}-\varphi_r$ curves in HF at Pt, Rh and Ir (Fig. 4A, B, C, curves 1) shows that the amounts of adsorbed fluoride anions at φ_r of the hydrogen and "double layer" regions are greater at Rh and Ir than at Pt, the $\Gamma_{F^-}^{max}$ (Rh) value being approximately equal to $\Gamma_{F^-}^{max}$ (Ir). The decrease of Γ_{F^-} at Rh and Ir starts at more cathodic φ_r values than at Pt. This is evidently due to the fact that the p.z.c. of Rh and Ir are more negative than the p.z.c. of Pt (by $\simeq 200$ mV, see below) and that the bond energy of adsorbed oxygen with Rh and Ir surfaces is higher than with Pt. The latter circumstance follows both from the electrochemical data, which show that oxygen adsorption on Rh and Ir occurs at more negative φ_r than on Pt, and from the comparison of the standard heats of formation of oxides[29], the heats of oxygen chemisorption on Pt, Rh and Ir and the bond energies Pt–O, Rh–O, Ir–O, calculated by the Pauling method[30,31].

Since in the solutions of acidified salts HA + CA at $[C^+] \gg [H^+]$, $\Gamma_{H^+} = \varepsilon$, the

curves of Fig. 5 express the dependence of the density of the surface free charge on potential. It is clear from Fig. 5 that at Pt at $\varphi_r > 300$ mV and at Rh and Ir over the whole range of φ_r being considered (50–800 mV) the values of ε at φ_r = constant in HF + KF are appreciably less than in $H_2SO_4 + Na_2SO_4$. The intersection of the ε–φ_r curve with the abscissa axis determines the value of the potential of the zero free charge ($\varphi_{r,\varepsilon=0}$). The values of $\varphi_{\varepsilon=0}$ (referred to NHE) of Pt, Rh and Ir electrodes in 0.3 *M* HF + 0.12 *M* KF (pH = 2.4) are listed in Table 1 which for comparison shows also the values of $\varphi_{\varepsilon=0}$ for 0.005 *M* H_2SO_4 + 0.5 *M* Na_2SO_4 (pH = 2.4), taken from the literature.

TABLE 1

THE VALUES OF $\varphi_{\varepsilon=0}$, $\varphi_{Q=0}$ AND $\Delta\sigma_{max}$ OF Pt, Rh AND Ir ELECTRODES

Solution	*Electrode*	$\varphi_{\varepsilon=0}/mV$	$\varphi_{Q=0}/mV$	$\Delta\sigma_{max}/erg\ cm^{-2}$
0.3 *M* HF + 0.12 *M* KF (pH = 2.4)	Pt	185	235	0
	Rh	−5	85	0
	Ir	−10	—	—
0.005 *M* H_2SO_4 + 0.5 *M* Na_2SO_4 (pH = 2.4)	Pt	160[b]	200[a]	—
	Rh	−40[c]	25[a]	—
	Ir	−60[d]	—	—
0.005 *M* H_2SO_4 + 0.06 *M* K_2SO_4 (pH = 2.4)	Pt	—	205	−15
	Rh	—	30	−60
0.01 *M* HCl + 0.12 *M* KCl (pH = 2.2)	Pt	—	130	−80

[a] The data of ref. 32 were slightly corrected.
[b] The data from ref. 32.
[c] The data from ref. 33.
[d] The data from ref. 34.

As can be seen from the Table, the values of $\varphi_{\varepsilon=0}$ for the three metals in HF + KF are all more positive or less negative than in $H_2SO_4 + Na_2SO_4$.

Thus the adsorbability of fluoride anions on Pt, Rh and Ir is substantially less than that of sulfate anions. When passing from Pt to Rh and Ir, there is a significant shift of $\varphi_{\varepsilon=0}$ as well as of the potentials of the transition from hydrogen to oxygen adsorption in the cathodic direction. It should be pointed out also that the adsorption properties of Rh and Ir electrodes in HF solutions at $\varphi_r < 400$ mV are similar.

(2). On the dependence of the reversible surface work on the potential of Pt and Ir electrodes

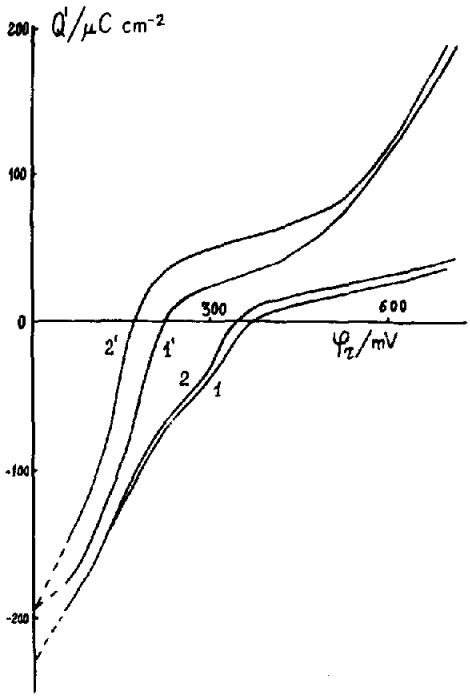
In connection with the lesser adsorbability of fluoride anions, as compared to sulfate anions, at Pt and Rh, it was of interest to calculate the $\Delta\sigma$–φ curves of the first kind[36] of Pt and Ir electrodes in acidified fluoride solutions and to compare them with those in acidified sulfate solutions[22,35].

The $\Delta\sigma$–φ curves of the first kind was calculated and plotted in the same manner as in ref. 36, using the Lippmann equation:

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{H^+},\mu_{CA}} = \Gamma_H = -Q' \qquad (3)$$

where σ is the reversible surface work, Γ_H the Gibbs hydrogen adsorption, Q' the total surface charge at constant μ_H[11,36]. Figure 6 shows as an illustration the Q'–φ_r curves of Pt and Rh electrodes in 0.3 *M* HF + 0.12 *M* KF solutions (curves 1 and 1') and in 0.005 *M* H_2SO_4 + 0.06 *M* K_2SO_4 (curves 2 and 2'). In order to pass from the Q–φ_r curves (similar to the curves in Fig. 3) to the Q'–φ_r curves, the solutions being investigated were substituted under isoelectric conditions by the 0.01 *M* HCl + 1 *M* KCl solution for which the Q'–φ_r curves at Pt and Rh are known[32,37]. Figure 8 shows the $\Delta\sigma$–φ curves of Pt and Rh electrodes in HF + KF and $H_2SO_4 + K_2SO_4$ solutions calculated from eqn. (3) by integration of the corresponding Q'–φ_r curves. As the integration constants for plotting the σ–φ curves are not known, the value of σ at the maximum of the curves for HF + KF is conditionally taken to be zero. The potentials of the zero total charge of the Pt and Rh electrodes surface, corresponding to the intersection of the Q'–φ_r curves with the abscissa axis and the relevant maximum values of $\Delta\sigma$ are listed in Table 1.

It is clear from Fig. 7 and Table 1 that when passing from $H_2SO_4 + K_2SO_4$ to HF + KF solutions, both at Pt and Rh $\varphi_{Q=0}$ and the left-hand branches of the curves shift in the anodic direction and σ_{max} increases. This supports the conclusion made earlier about the lesser adsorbability of fluoride anions at Pt and Rh, as compared to sulfate anions.



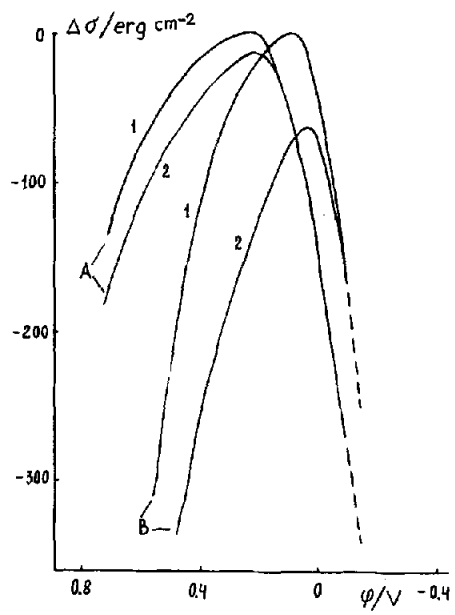


Fig. 6. Q'–φ_r curves of (1,2) Pt and (1',2') Rh electrodes in solutions: (1) 0.3 *M* HF + 0.12 *M* KF; (2) 0.005 *M* H_2SO_4 + 0.06 *M* K_2SO_4.

Fig. 7. Curves of the dependence of the reversible surface work of (A) Pt and (B) Rh electrodes on the potential (electrocapillary curves of the 1st kind) in solutions: (1) 0.3 *M* HF + 0.12 *M* KF; (2) 0.005 *M* H_2SO_4 + 0.06 *M* K_2SO_4.

The comparison of the $\Delta\sigma$–φ curves for Pt and Rh with the σ–φ curves for Hg shows that at Pt and Rh electrodes the change of σ when passing from fluoride to sulfate and chloride anions is greater than on Hg. Thus, if for Hg the change in the maximum values of σ when passing from fluoride to chloride (0.1 *M* solutions) is less than 3 erg cm^{-2} for Pt it is *ca.* 80 erg cm^{-2}. These differences are explained by the partial charge transfer of specifically adsorbed ions to the metal surface at Pt and Rh[10,25,38].

It should be pointed out that there are certain differences in the $\Delta\sigma$–φ curves at Pt and Rh. At Rh the difference between the values of $\varphi_{Q=0}$ and σ_{max} (see Table 1) for HF + KF and $H_2SO_4 + K_2SO_4$ solutions is much larger than at Pt. This appears to be due to a greater difference in the adsorbability of fluoride and sulfate anions at Rh than at Pt. A faster decrease of the left-hand branches of the curves at Rh than at Pt can be explained by the larger value of $d\theta_O/d\varphi$ (θ_O is the surface coverage with O_{ads}) at the Rh electrode in the range of φ values studied, which leads to an increase of $|d\sigma/d\varphi|$. A significant shift in the values of $\varphi_{Q=0}$ in the cathodic direction when passing from Pt to Rh is due to a much earlier oxygen deposition on Rh.

(3). The potentiodynamic curves

The potentiodynamic curves of Pt, Rh and Ir electrodes in 0.14 *M* HF (curves 1) and 0.02 *M* H_2SO_4 solutions (curves 2) with similar pH values are compared in Fig. 8 (refs. 21, 22, 35). At the Pt/Pt electrode the second peak corresponding to more

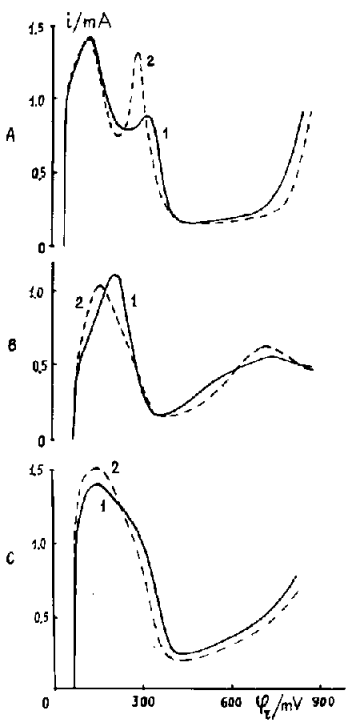


Fig. 8. Potentiodynamic curves of (A) Pt, (B) Rh and (C) Ir electrodes in solutions: (1) 0.14 *M* HF; (2) 0.02 *M* H_2SO_4.

strongly bound hydrogen is much higher in H_2SO_4 than in HF. At the same time, the ionization of a part of the strongly bound hydrogen occurs in HF at higher φ_r values than in H_2SO_4. The comparison of the potentiodynamic curves shows that in the presence of fluoride anions, the total amount of H_{ads} on the Pt electrode surface is the same as in the presence of sulfate anions. Consequently, the decrease in the height of the second peak in HF, as compared to H_2SO_4, is associated with its broadening owing to the ionization of a part of the strongly bound hydrogen at larger φ_r. The shift of the ionization potentials of the strongly bound hydrogen in the anodic direction in HF, as compared to H_2SO_4, points to an increase in HF of the bond energy of this form of H_{ads}.

At Rh and Ir in HF (Fig. 8, B, C, curves 1), just as in H_2SO_4, the potentiodynamic curves show one maximum, which testifies to the presence at $\varphi_r \geqslant 0$ of only one form of H_{ads}[39,40]. The ionization regions of adsorbed hydrogen at Rh and Ir in HF are also shifted in the anodic direction, as compared to H_2SO_4, which is an indication of an increase in the bond energy of H_{ads} at these metals in the presence of fluoride anions as well. These results agree with the expected effect of the decrease of the anion adsorbability on the bond energy of the dipoles Rh–H_{ads}, Ir–H_{ads} and Pt–H_{ads} (strongly bound form), turned with their negative ends towards the solution[36,37].

The potentiodynamic curves also confirm an earlier oxygen deposition at Pt, Rh and Ir in HF solutions as compared to H_2SO_4.

SUMMARY

The charging curves, the potentiodynamic curves and the isoelectric potential shifts have been measured on Pt, Rh and Ir electrodes in HF and HF + KF solutions in a Teflon cell. From the obtained data, the Γ_{H^+}–φ curves and the $\Delta\sigma$–φ curves of the first kind have been calculated by means of the thermodynamic theory of the hydrogen electrode. The Γ_{H^+} values in 0.14 *M* HF and 0.3 *M* HF + 0.12 *M* KF are much less than in 0.005 *M* H_2SO_4 and 0.005 *M* H_2SO_4 + 0.5 *M* K_2SO_4 solutions. In the presence of F^- anions, the potentials $\varphi_{\varepsilon=0}$ and $\varphi_{Q=0}$ are by 25–55 mV more anodic than in the presence of SO_4^{2-} anions. In an acidified fluoride solution the values of σ are higher than in an acidified sulfate solution. The analysis of the results obtained leads to the conclusion that on platinum metals the fluoride anions in the φ_r region investigated (from $\varphi_r = 0$ to $\varphi_r = 900$ mV) are the most weakly adsorbed anions.

REFERENCES

1 A. D. Obrucheva, *Zh. Fiz. Khim.*, 32 (1958) 2155.
2 P. V. Popat and N. Hackerman, *J. Phys. Chem.*, 62 (1958) 1198.
3 N. A. Balashova and V. E. Kazarinov, *Elektrokhimiya*, 1 (1965) 512.
4 V. E. Kazarinov, *Elektrokhimiya*, 2 (1966) 1389.
5 Y. C. Chiu and M. A. Genshaw, *J. Phys. Chem.*, 73 (1969) 3571.
6 B. I. Podlovchenko, V. F. Stenin and A. N. Frumkin, *Elektrokhimiya*, 8 (1972) 129.
7 A. N. Frumkin and A. I. Shlygin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 5 (1936) 773; Acta Physicochim. URSS. 5 (1936) 819.
8 A. N. Frumkin, N. A. Balashova and V. E. Kazarinov, *J. Electrochem. Soc.*, 113 (1966) 1011.

9 A. N. Frumkin, O. A. Petrii and R. V. Marvet, *Elektrokhimiya*, 3 (1967) 116; *J. Electroanal. Chem.*, 12 (1966) 504.
10 A. N. Frumkin, O. A. Petrii, A. M. Kossaya, V. S. Entina and V. V. Topolev, *J. Electroanal. Chem.*, 16 (1968) 175.
11 A. N. Frumkin, O. A. Petrii and B. B. Damaskin, *Elektrokhimiya*, 6 (1970) 614; *J. Electroanal. Chem.*, 27 (1970) 81.
12 B. B. Damaskin, O. A. Petrii and V. V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York–London, 1971, Ch. 9.
13 S. Ya. Vasina and O. A. Petrii, *Elektrokhimiya*, 6 (1970) 242.
14 A. N. Frumkin, *Advan. Electrochem. Electrochem. Eng.*, 3 (1963) 287.
15 M. R. Tarasevich, K. A. Radyushkina and R. Kh. Burshtein, *Elektrokhimiya*, 3 (1967) 455.
16 A. D. Semenova, A. I. Pletyushkina and G. D. Vovchenko, *Vestn. Mosk. Univ., Ser Khim.*, No. 4, (1968) 45.
17 B. I. Podlovchenko and R. P. Petukhova, *Elektrokhimiya*, 5 (1969) 380; 6 (1970) 198.
18 O. A. Petrii, A. M. Kossaya-Tsybulevskaya and Yu. M. Tyurin, *Elektrokhimiya*, 3 (1967) 617.
19 L. Aliua and B. I. Podlovchenko, *Elektrokhimiya*, 9 (1973) 1218.
20 B. I. Podlovchenko and N. A. Epshtein, *Elektrokhimiya*, 8 (1972) 613.
21 N. A. Epshtein and B. I. Podlovchenko, *Elektrokhimiya*, 9 (1973) 779.
22 B. I. Podlovchenko and N. A. Epshtein, *Elektrokhimiya*, 9 (1973) 1194.
23 *Spravochnik Khimika, Vol. 3*, Khimiya, Moscow–Leningrad, 1965, p. 593.
24 N. A. Balashova and V. E. Kazarinov, *Usp. Khim.*, 34 (1965) 1721.
25 O. A. Petrii, A. N. Frumkin and V. V. Topolev, *Elektrokhimiya*, 5 (1969) 1104.
26 V. V. Topolev and O. A. Petrii, *Elektrokhimiya*, 6 (1970) 1726.
27 O. A. Petrii, V. E. Kazarinov and I. G. Shchigorev, *Elektrokhimiya*, 6 (1970) 1565.
28 V. E. Kazarinov, O. A. Petrii, V. V. Topolev and A. V. Losev, *Elektrokhimiya*, 7 (1971) 1365.
29 G. Samsanov (Ed.), *Fisiko-Khimicheskie Svoistva Okislov*, Metallurgiya, Moscow, 1969, pp. 46, 48.
30 D. Brennan, D. O. Hayward and B. M. Trapnell, *Proc. Roy. Soc.*, A256 (1960) 81.
31 I. G. Frith and H. B. Holland, *Trans. Faraday Soc.*, 65 (1969) 1121.
32 O. A. Petrii, A. N. Frumkin and Yu. G. Kotlov, *Elektrokhimiya*, 5 (1969) 476; 6 (1970) 725.
33 A. N. Frumkin, O. A. Petrii and A. M. Kossaya, *Elektrokhimiya*, 4 (1968) 475.
34 O. A. Petrii and Nguen van Tue, *Elektrokhimiya*, 5 (1969) 494.
35 B. I. Podlovchenko and N. A. Epshtein, *Elektrokhimiya*, 8 (1972) 1522.
36 A. N. Frumkin and O. A. Petrii, *Dokl. Akad. Nauk SSSR*, 196 (1971) 1387.
37 A. Frumkin and O. Petrii, *Electrochim. Acta*, 15 (1970) 391.
38 B. B. Damaskin, *Elektrokhimiya*, 6 (1970) 1135.
39 O. A. Petrii, A. N. Frumkin and Yu. G. Kotlov, *Elektrokhimiya*, 5 (1969) 735.
40 O. A. Petrii and Nguen van Tue, *Elektrokhimiya*, 6 (1970) 408.