STUDY OF THE SURFACE STATE OF AN IRIDIUM ELECTRODE BY THE METHOD OF ISOELECTRIC POTENTIAL SHIFTS

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In [1] the adsorption properties of an iridium electrode were studied in the solutions 0.01 N H_2SO_4 + 1 N Na_2SO_4, 0.01 N HCl + 1 N KCl, and 0.01 N KOH + 1 N KCl. In the present paper results are presented of studies of the behavior of an iridium electrode in the solutions 0.01 N KOH, 0.01 N KOH + 1 N KBr, 0.01 N KOH + 1 N KI, and 0.01 N HBr + 1 N KBr.

The measuring technique, the preparation of the iridium electrode, and the determination of its true surface area were described in [1]. The isoelectric potential shifts [2, 3] were determined, either by replacing 0.001 N KOH with 0.1 N KOH, or by replacing 0.001 N KOH (or HBr) + 0.009 N KI (or KBr) with 0.1 N KOH (or HBr) + 0.91 N KI (or KBr). The experiments were carried out at 20 ± 1°C. The potentials φ_r refer to a reversible hydrogen electrode in the same solution, the potentials φ to the n.h.e.

Curves of isoelectric potential shifts of the iridium electrode in the systems studied are shown in Fig. 1. At small polarizations the behavior of the iridium electrode approaches that of a reversible hydrogen electrode at constant partial pressure of hydrogen. In alkaline solution, such behavior of the electrode is practically maintained over the entire potential range studied when no salt is added. In other cases the isoelectric shifts deviate from −1 at anodic φ_r, and they do this more the higher the specific adsorbability of the base electrolyte anion. However, even in 0.01 N HBr + 1 N KBr the magnitude of the shift does not reach zero, which would correspond to the absence of adsorbed hydrogen and oxygen on the surface [2].

Thus, on iridium the adsorption regions of hydrogen and oxygen overlap more or less in all the solutions studied. Only in acidified bromide solution is there a narrow potential region (from 0.4 to 0.5 V) which to the best approximation can be considered a "double-layer" region of the iridium electrode. It is interesting to note that from the measured data of isoelectric potential shifts, the behavior of iridium in 0.01 N KOH + 1 N KI solution is close to that in 0.01 N HCl + 1 N KCl solution [1].

From the isoelectric potential shifts and equilibrium charging curves, the potential dependence of hydrogen ion adsorption, Γ_{H^+}, was calculated. This was done following Eqs. (1) (for the alkaline solution without the addition of neutral salt) and (2) [4]:

$$(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu^{\pm}_{COH}} = \frac{1}{2}(\partial\varphi_r/\partial\mu^{\pm}_{COH})_Q\,(\partial Q/\partial\varphi_r)_{\mu^{\pm}_{COH}}, \quad (1)$$

$$(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{OH^-},\,\mu_{CA}} = (\partial\varphi_r/\partial\mu_{OH^-})_{Q,\,\mu_{CA}}\,(\partial Q/\partial\varphi_r)_{\mu_{OH^-},\,\mu_{CA}}, \quad (2)$$

where Q is the total surface charge density; μ_{OH^-} and $\mu^{\pm}_{COH}$ are the chemical potential of OH^- ions and the mean chemical potential of the ions of the base; μ_{CA} is the chemical potential of the ions of the salt. In Fig. 2 the computed dependences are compared with those found by experiment from titrating the solution [3]. The experimental Γ_{H^+} values designated with a special symbol in Fig. 2 were used as integration constants for the calculation following Eqs. (1) and (2). The coincidence of computed and experimental $\Gamma_{H^+} - \varphi_r$ curves means that the systems studied are reversible over the entire φ_r interval studied.

The practical independence of Γ_{H^+} on φ_r at the iridium electrode in alkaline solution without salt addition attracts attention. In agreement with [4, 5] this can be considered as the result of accidental compensation of two

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TABLE 1

Electrode	Solution	$\varphi_{Q=0}$, mV (vs. nhe)	φ_{zc} (acc. to our meas. and [11, 12]), in mV (vs n.h.e.)	φ_{zc} (according to [14]), in mV (vs n.h.e.)
Ir	1 *N* Na_2SO_4 + 0,01 *N* H_2SO_4 (pH 2,4)	95		~90
	1 *N* K_2SO_4 + H_2SO_4 (pH 2,4)			
	1 *N* KBr + 0,01 *N* HBr	−30	−120	~−60
	1 *N* KBr + H_2SO_4 (pH 2)			
Rh	1 *N* Na_2SO_4 + 0,01 *N* H_2SO_4 (pH 2,4)	50	−60	~30
	1 *N* K_2SO_4 + H_2SO_4 (pH 2,4)			
	1 *N* Na_2SO_4 + 0,01 *N* NaOH	−400	—	~−470
	1 *N* K_2SO_4 + 0,01 *N* NaOH			
Pt	1 *N* Na_2SO_4 + 0,01 *N* H_2SO_4 (pH 2,4)	240	160	~100
	0,1 *N* K_2SO_4 + H_2SO_4 (pH 2,4)			
	1 *N* KCl + 0,01 *N* HCl	140	40	80
	0,1 *N* KCl + HCl (pH 2)			
	1 *N* KBr + 0,01 *N* HBr	55	−30	−10
	0,1 *N* KBr + H_2SO_4 (pH 2)			
	1 *N* Na_2SO_4 + 0,01 *N* NaOH	−250	—	−340
	0,1 *N* K_2SO_4 + 0,01 *N* NaOH			

effects: the adsorption of cations at the expense of ionization of adsorbed hydrogen, which falls with increasing φ_r, and the adsorption of hydrated oxide groups, which increases with φ_r. The second form of cation adsorption can evidently, as on platinum, be represented as the adsorption of anions of the type OK^-. The addition of specifically adsorbing anions leads to the expulsion of OK^- anions from the surface and a change in the shape of the $\Gamma_{H^+} - \varphi_r$ curve. We note that on platinum, in contrast to iridium, some change in Γ_{H^+} with potential is always observed.

In solutions containing excess indifferent electrolyte, Γ_{H^+} can be equated to the charge density on the metal side of the electric double layer [6]. In this case the potentials corresponding to the condition $\Gamma_{H^+} = 0$ are the potentials of zero charge φ_{zc}. From the measurements reported it follows that in iodide solutions made alkaline, there are two points of zero charge, which are at $\varphi_r = 0.11$ V and 0.75 V, respectively. The first corresponds to the reduced, the other to the oxidized surface state. The point of zero charge for an oxidized surface was previously observed in equilibrium measurements of Γ_{H^+} in acidified KCl solutions on ruthenium [7, 8]. On platinum it was found when determining the electrokinetic potential in very dilute acid solutions [9] and from measurements of the potential dependence of surface tension by Gokhshtein's method [10]. In the case of the iridium electrode it is possible to observe at once two points of zero charge under conditions where the system is in equilibrium over the entire potential range.

Measurements in iodide solutions with different alkali concentrations allowed us to obtain data on the pH dependence of φ_{zc} (Fig. 3). Both the φ_{zc} (as referred to a constant reference electrode) shift with increasing pH to the negative side. The shift of the first φ_{zc} is about 45 mV per pH unit; that of the second is about 180 mV. The pH dependence of the potentials of constant double-layer charge, including φ_{zc}, was discussed in [11, 12]. A comparison of the data from those papers and the present work shows that the sign of $(\partial\varphi/\partial\mu_{H^+})\Gamma_{H^+}$ on iridium is the same as on platinum and rhodium. From this one can conclude that the dipoles of adsorbed hydrogen and oxygen on iridium are also oriented with the negative end to the solution. An appreciably larger shift of the potential of constant double-layer charge on the descending branch of the $\Gamma_{H^+} - \varphi_r$ curve was also observed on platinum and rhodium in [12], where the nature of this phenomenon was discussed.

It was pointed out in [5, 11] that for the platinum metals one can, besides φ_{zc}, refer to potentials $\varphi_{Q=0}$ which correspond to zero total surface charge. For platinum and rhodium $\varphi_{Q=0}$ were determined in [11, 12]. In order to determine $\varphi_{Q=0}$ one must find a solution where in a given potential range the entire quantity of electricity supplied is exclusively used for charging the capacity of the electric double layer. On iridium the closest approach to such a surface state exists in acidified bromide solution, as shown above; this makes it possible to give a rough estimate of $\varphi_{Q=0}$. To this end an $A_H - \varphi_r$ curve for the solution 0.01 N HBr + 1 N KBr was constructed according to the equation [6]

$$A_H = \Gamma_{H^+} - Q, \tag{3}$$

where A_H is the quantity of adsorbed atomic hydrogen per square centimeter of surface area in electrical units. The

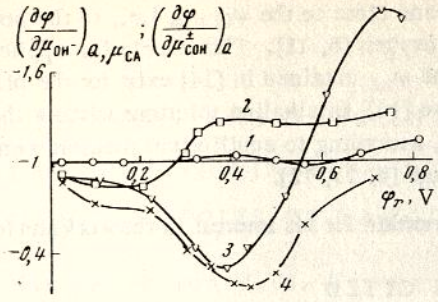

Fig. 1

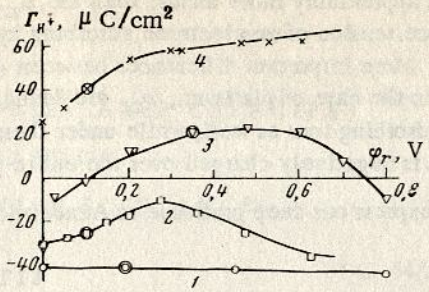

Fig. 2

Fig. 1. Potential dependence of the isoelectric potential shifts for an iridium electrode in the solutions: 1) 0.01 N KOH; 2) 0.01 N KOH + 1 N KBr; 3) 0.01 N KOH + 1 N KI; 4) 0.01 N HBr + 1 N KBr.

Fig. 2. Potential dependence of hydrogen ion adsorption for an iridium electrode in the solutions: 1) 0.01 N KOH; 2) 0.01 N KOH + 1 N KBr; 3) 0.01 N KOH + 1 N KI; 4) 0.01 N HBr + 1 N KBr.

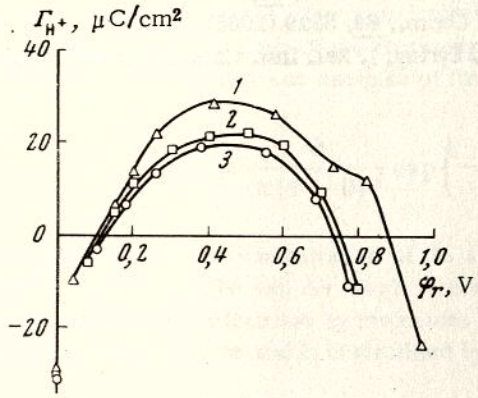

Fig. 3

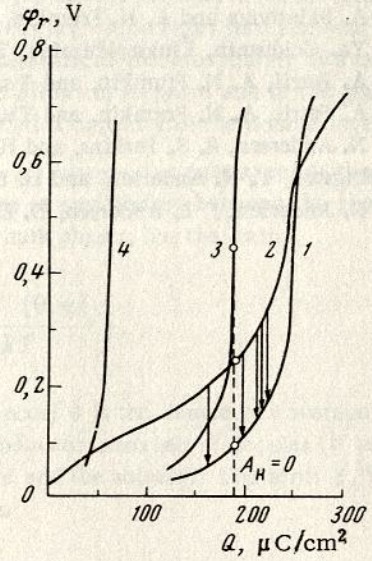

Fig. 4

Fig. 3. Potential dependence of hydrogen ion adsorption at an iridium electrode in the solutions: 1) 0.001 N KOH + 1 N KOH; 2) 0.01 N KOH + 1 N KI; 3) 0.02 N KOH + 1 N KI.

Fig. 4. Determination of the potentials corresponding to zero total surface charge of the iridium electrode: 1) the charging curve in 0.01 N HBr + 1 N KBr; 2) the charging curve in 0.01 N H_2SO_4 + 1 N Na_2SO_4; 3) the $A_H - \varphi_r$ curve in 0.01 N HBr + 1 N KBr; 4) the $\Gamma_{H^+} - \varphi_r$ curve in 0.01 N HBr + 1 N KBr.

isoelectric potential shifts were then measured for the substitution of 0.01 N H_2SO_4 + 1 N Na_2SO_4 by 0.01 N HBr + 1 N KBr, and in this way points on the charging curves were found which correspond to the same Q in both solutions. These points are connected with vertical arrows in Fig. 4. The vertical line drawn from the point at φ_r = 0.45 V on the $A_H - \varphi_r$ curve in bromide solution intersects the charging curve in bromide solution at φ_r = 90 mV, but that in sulfate solution at φ_r = 240 mV. These potentials are also the $\varphi_{Q=0}$ in the systems studied. In sulfate solutions, $\varphi_{Q=0}$ for iridium is 40 mV more positive than that for rhodium. The $\varphi_{Q=0}$ potentials on iridium as well as those on the other platinum metals [11, 12] lie at more anodic potentials than the φ_{zc}.

In [13] a method for determining φ_{zc} was proposed which is based on measuring the potential of a rapidly scraped electrode surface at open circuit. In [14] φ_{zc} for an iridium electrode was measured by this method. A comparison of these potentials with the data obtained by us (Table 1) shows that actually the potentials reported

in [14] are appreciably more anodic than the φ_{zc} of iridium and close to the $\varphi_{Q=0}$, i.e., to the potentials of maximum surface tension of an electrode adsorbing hydrogen and oxygen [5, 11]. This conclusion applies to the rhodium electrode. More important differences between $\varphi_{Q=0}$ and the φ_{zc} obtained in [14] exist for the platinum electrode. However, in the case of platinum, φ_{zc} are found, according to [14], in alkaline solutions without the addition of specifically adsorbing ions as well, while under these conditions, according to equilibrium measurements, the surface of the metals is negatively charged over the entire potential range [4, 11, 12].

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