DETERMINATION OF THE RELATIONS BETWEEN THE ADSORPTION OF HYDROGEN IONS ON IRIDIUM AND SOLUTION pH WITH A REVERSIBLE HYDROGEN POTENTIAL

R. Notoya and O. A. Petrii

UDC 541.135.52.93-183

The method of potentiometric titration with a large indicator electrode was first proposed for the investigation of the structure of the electric double layer on platinum metals by Frumkin and Shlygin [1, 2] and has again become of significance in the light of the thermodynamic theory of the platinum electrode [3, 4] and in relation to the development of a method of potentiometric titration under isoelectric conditions [5, 6]. This method has been used in [7, 8] with platinized platinum (Pt/Pt) and rhodium plated platinum (Rh/Pt) electrodes for determination of $\Delta\sigma, \varphi$ curves with a reversible hydrogen potential, where σ is the reversible work function and φ is the electrode potential.

In the present work the potentiometric titration method has been used for obtaining similar relations for an iridium electrode. The experimental method and cell were the same as in [7] with the exception that in this case the titration was carried out automatically by the use of an automatic titrator manufactured by "Hiranum" (Japan). This instrument provides a means of adding a total of 0.05 ml of the titrating solution and to select intervals of 1 h between additions. The tests were performed at a temperature of 25 ± 0.5°C with an atmospheric hydrogen pressure. The large indicator electrode was an iridium plated platinum gauze with an apparent surface area of 90 cm². The iridium plating was accomplished from a 2% solution of Na_2IrCl_4 acidified with 0.1 N HCl. The actual surface area of the large indicator electrode was determined by hydrogen adsorption by the method proposed in [9] as about 2 m² and remained unchanged with time.

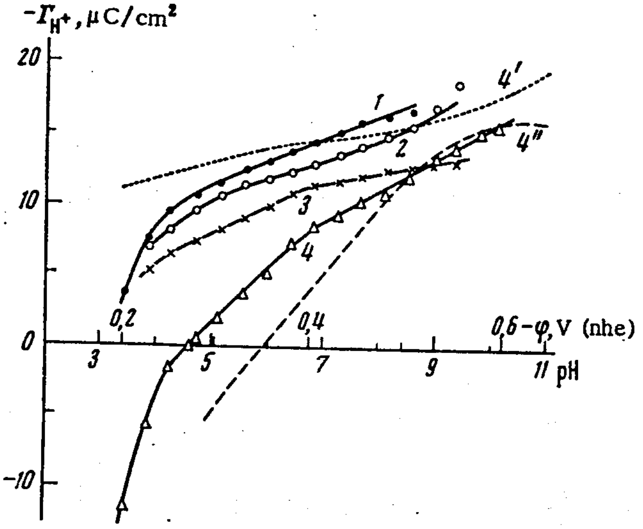

Fig. 1. Relations between the adsorption of hydrogen ions with a reversible hydrogen potential and the solution pH on Ir in: 1) 0.1 N Cs_2SO_4; 2) Na_2SO_4; 3) NaCl; 4) NaBr; 4') on Pt in 0.1 N NaBr; 4") on Rh in 0.1 N NaBr

---

Institute of Catalysis, Hokkaido University, Sapporo, Japan. Moscow State University, USSR. Translated from Elektrokhimiya, Vol. 12, No. 4, pp. 655-657, April, 1976. Original article submitted July 3, 1975.

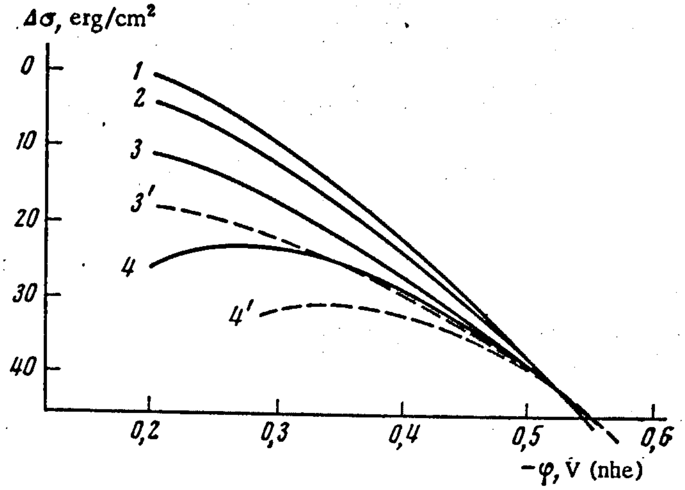

Fig. 2. Electrocapillary curves of the second type for Ir in: 1) 0.1 N Cs_2SO_4; 2) Na_2SO_4; 3) NaCl; 4) NaBr; 3') on Rh in 0.1 N NaCl; 4') on Rh in 0.1 N NaBr.

Figure 1 shows the relation between the free surface loading Γ_{H^+} [3] and solution pH with a reversible hydrogen potential in solutions of 0.1 N Cs_2SO_4, Na_2SO_4, NaCl, and NaBr. In the presence of Cs^+ ions in sulfate solutions $|\Gamma_{H^+}|$ is greater than in the presence of Na^+ ions. From the condition of electrical neutrality in the solutions with the same surface inactive anions the difference of $|\Gamma_{H^+}|$ is equal to the difference of Γ_{C^+} where C^+ represents the cation. Therefore the value Γ_{C^+} increases in passing from Na^+ to Cs^+ and indicates the specific adsorption of Cs^+ cations on iridium. A similar effect has been observed for Pt and Rh electrodes [7, 8]. The decrease of $|\Gamma_{H^+}|$ in passing along the series Na_2SO_4 > NaCl > NaBr is caused by the increase in specific adsorption of anions in the series $SO_4^{2-} < Cl^- < Br^-$.

In accordance with the theory of the double layer on metals of the platinum group [3] the slopes of the linear parts of the Γ_{H^+}/φ curves may be used to calculate the equilibrium capacity C_D of the electric double layer in the presence of an excess of salt. In a solution of 0.1 N Na_2SO_4 C_D was equal to about 22 μF/cm². This value is somewhat greater than on Pt (11-12 μF/cm²) [7] and Rh (16-17 μF/cm²) [8] electrodes. It is possible that this difference is related to the inaccuracy of the determination of the true surface of the iridium plated electrode for the method used by the authors. For this reason it is difficult also to compare absolute values of Γ_{H^+} on different metals although in accordance with Fig. 1 at a pH < 8, $|\Gamma_{H^+}|$ decreases in the order Pt < Ir < Rh. But doubt is not caused by the fact that (Fig. 1) the null free charge potential is close to that of Rh, which was concluded also from earlier determinations of the null free charge potential in solutions with constant pH [10]. The null free charge potential of iridium with an atmospheric pressure of hydrogen is equal to −0.27 V relative to a normal hydrogen electrode in 0.1 N NaBr.

The data in Fig. 1 were used to calculate the relations between the reversible work function σ and φ at a constant hydrogen pressure in the system. These are the electrocapillary curves of the second type [4]. The $\Delta\sigma, \varphi$ curves obtained are shown in Fig. 2. In a comparison of the $\Delta\sigma, \varphi$ curves in different solutions it is assumed that at pH 9 the values of Δσ coincide. This assumption is not completely accurate for Rh and Ir since the values of Γ_{H^+} in the presence of the SO_4^{2-}, Cl^-, and Br^- ions do not coincide at pH $\geq$ 9 in contrast to the data for Pt [7]. The reasons for this effect are not clear.

The nature of the positions of the $\Delta\sigma, \varphi$ curves and the differences in σ for different solutions are close to those found earlier for Rh [8].* This indicates the similar adsorption properties of iridium and rhodium in relation to anions.

The authors express their deep gratitude to Academician A. N. Frumkin and to Professor A. Matsude for their participation in discussions of the results and valuable comments.

---

*The positions of the $\Delta\sigma, \varphi$ curves in Fig. 2 are arbitrary since the absence of an integration constant makes it possible only to compare the differences Δσ in different solutions on Rh and Ir.

LITERATURE CITED

1. A. N. Frumkin and A. I. Shlygin, Izv. Akad. Nauk SSSR, Otd. Matem. i Estestv. N. 773 (1936); Acta Physicochim. URSS, 5, 819 (1936).
2. A. I. Shlygin, Izv. Akad. Nauk KazSSR, Ser. Khim., No. 3, 6 (1949).
3. A. N. Frumkin, O. A. Petrii, and B. B. Damaskin, Élektrokhimiya, 6, 614 (1970).
4. A. N. Frumkin and O. A. Petrii, Dokl. Akad. Nauk SSSR, 196, 1387 (1971).
5. A. N. Frumkin, O. A. Petrii, and T. Ya. Kolotyrkina, Élektrokhimiya, 11, 1741 (1974).
6. A. N. Frumkin, O. A. Petrii, and T. Ya. Kolotyrkina-Safonova, Dokl. Akad. Nauk SSSR, 222, 1159 (1975).
7. R. Notoya, O. A. Petrii, S. Ya. Vasina, and A. N. Frumkin, Élektrokhimiya, 8, 907 (1972).
8. O. A. Petrii and T. Ya. Kolotyrkina, Élektrokhimiya, 9, 254 (1973).
9. A. D. Semenova, G. P. Khomchenko, and G. D. Vovchenko, Vestn. Mosk. Un-ta, Ser. Khim., No. 3, 75 (1969).
10. O. A. Petrii and Nguen van Tie, Élektrokhimiya, 5, 494 (1969).

INFLUENCE OF THE RATE OF MOVEMENT OF SOLUTIONS OF ELECTROLYTES ON THEIR ELECTRIC CONDUCTIVITY

G. I. Volkov

UDC 541.138

In the intensification of processes of electrolysis, sometimes high rates of motion of the solution of the electrolyte are used. However, it is unknown whether in this case the electric conductivity is changed in the presence of the substantial turbulence of the flow.

To verify the existence of such an effect, we conducted experiments according to the following procedure. Two glass vessels were connected with a glass tube with inner diameter 4.0 mm, 53 mm long. The vessels contained 1% zinc amalgam, which served as a current lead and for measurement of the potential difference. Under the conditions of the experiments these electrodes were practically nonpolarized. The current strength was measured with an M-82 milliammeter, and the voltage with an M-106 voltmeter. The direct current source was a VSA-5A rectifier.

The solution of the electrolyte was pumped over with a centrifugal titanium pump from one container into another through glass vessels and glass tubing connecting them. The rate of delivery of the electrolyte solution was measured with a rotameter. The experiments were conducted at room temperature. Since an appreciable portion of the current passed through

TABLE 1. Influence of the Rate of Motion of Solutions of Electrolytes on Their Electric Conductivity

Electrolyte	Soln. motion (v, m/sec) and Reynolds value (Re)			
	$v=15{,}4$; Re=61 700	$v=16{,}3$; Re=65 200	$v=17{,}2$; Re=68 900	$v=19{,}0$; Re=76 000
0,1 *N* HCl	0,93	0,88	0,84	0,79
0,1 *N* $ZnSO_4$	0,93	0,88	0,84	0,79
0,1 *N* LiCl	0,93	0,87	0,83	0,77
0,1 *N* NaOH	0,93	0,87	0,82	0,75
0,1 *N* $K_4Fe(CN)_6$	0,92	0,86	0,81	0,74
0,01 *N* $K_4Fe(CN)_6$	0,92	0,86	0,80	0,73

Moscow. Translated from Élektrokhimiya, Vol. 11, No. 4, pp. 658-659, April, 1976. Original article submitted February 12, 1975.