USE OF RADIOACTIVE INDICATORS TO DETERMINE THE RELATION BETWEEN THE PLATINUM NULL FREE CHARGE POTENTIAL AND THE pH OF THE SOLUTION

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UDC 541.138

The relation between the platinum null free charge potential (NFCP) and the solution pH was established in the experimental work of [1, 2] and then interpreted in terms of the thermodynamic theory of the platinum electrode in [2, 3]. From a study of adsorption curves and measurements on isoelectric potential shifts in acidified 1 N Na_2SO_4 (pH 1.5-3.0) solutions, it was reported that a 1 unit increase in pH would displace the NFCP toward the cathodic side by ~18 mV [2]. On the other hand, work with radioactive indicators in 10^{-3}-10^{-2} N Na_2SO_4 and Cs_2SO_4 solutions at pH 2-4 failed to disclose any such displacement of the NFCP, at least to within the limits of experimental error [1]. Since the measurements in question here were carried out on electrolyte which had been removed from the cell, it seemed of interest to restudy the relation between the NFCP of the platinized platinum electrode and the solution pH with the improved radiochemical techniques which are now available [4]. The present paper deals with this and the companion problem of measuring the adsorption of sodium, cesium, and sulfate ions over a wide range of potentials, working at pH's as close as possible to 7.

The cell used here was similar to that described earlier in [4]. The auxiliary electrode was placed in the solution with the working electrode, thus avoiding the necessity of carrying out pH measurements under polarization of the Pt/Pt electrode. The solution in the working portion of the cell was periodically replaced by fresh solution, being sucked off into a special container where its pH was measured with a glass electrode. A stream of argon was passed through the cell to keep the solution in continual agitation. The radioactivity of the electrode was measured after the circuit had been broken and a steady potential established.

Measurements were carried out on acidified sodium and cesium sulfate solutions of $4 \cdot 10^{-3}$ and 10^{-2} N total concentration. The best results were obtained at the $4 \cdot 10^{-3}$ N concentration. Participation of hydrogen ions in double layer formation had to be taken into account when determining the sodium and cesium ion adsorption at this concentration and pH 3, a correction based on the data of [5] being introduced.

The Pt/Pt electrode used here had an apparent surface area of 2 cm^2 and a true surface area of 1500-3000 cm^2; it was prepared by the procedure of [5]. The true surface area was determined from the hydrogen segment of a charging curve developed in 1 N H_2SO_4.

The labeled solutions were prepared from Na-22, Cs-134, and S-35. In what follows, φ_r will designate potentials measured with respect to a reversible hydrogen electrode placed in the working solution.

Figure 1 shows the effect of the potential on the adsorption of Na^+ (Γ_{Na^+}) and SO_4^{2-} ($\Gamma_{SO_4^{2-}}$) ions, similar relations for cesium sulfate solutions being shown in Fig. 2. With rising pH, the cation adsorption increased and the anion adsorption fell. The Γ_{Na^+} (Γ_{Cs^+}), φ_r and $\Gamma_{SO_4^{2-}}$, φ_r curves obtained here had the same form as those described earlier in [6, 7]. The fact that the cesium ions adsorbed more extensively than the sodium was due to the specific adsorption of the cesium on the platinum electrode [8-12]. This specific adsorption had, however, very little effect on the sulfate ion adsorption, the $\Gamma_{SO_4^{2-}}$, φ_r curves for the sodium and cesium sulfate solutions being essentially the same.

The NFCP in the sodium sulfate solution was read off from the point of intersection of the Γ_{Na^+}, φ_r

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M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 10, No. 9, pp. 1352-1355, September, 1974. Original article submitted October 8, 1973.

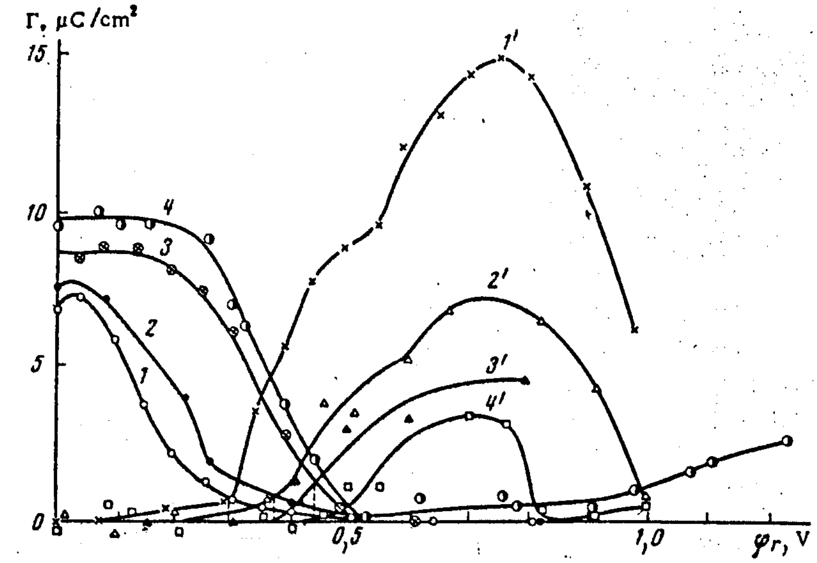

Fig. 1. Relation between the adsorption of sodium ions (1-4) or sulfate ions (1'-4') and potential on the Pt/Pt electrode in $4 \cdot 10^{-3}$ N ($Na_2SO_4 + H_2SO_4$) solutions with pH: 1, 1') 3.0; 2, 2') 3.9; 3, 3') 5.3; 4, 4') 6.2.

and $\Gamma_{SO_4^{2-}}$, φ_r curves; the fact that its value, 0.13 ±0.02 V (with respect to the NHE), proved to be practically unaffected by change in the pH was consistent with the results reported in [1]. It has been shown in [2] that the effect of increasing pH on the NFCP displacement becomes more pronounced as the specific adsorbability of the anion increases. This would be consistent with our failure to detect a variation of the NFCP with change in pH [3], the specific SO_4^{2-} adsorption being less in dilute solution than in 1 N Na_2SO_4. There was a displacement of the NFCP toward the anodic side with increasing pH in the cesium sulfate solutions, the value being 0.15 V at pH 3 and 0.22 V at pH 6. These effects clearly trace back to the specific adsorption of the cesium ions, which increases with increasing pH of the solution [9-12]. This aspect of the cesium ion adsorption also accounts for the fact that the NFCP was more positive in the presence of cesium ions than in the presence of sodium ions, especially at the higher pH values.

An equation relating the NFCP ($\varphi_{\Gamma_{H^+}=0} = 0$) to pH derived in [13] has the form

$$(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0} = \frac{(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r}}{(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r} - 1}, \tag{1}$$

A_H being the surface concentration of adsorbed atomic hydrogen and φ the potential with respect to the fixed reference electrode [all quantities in Eq. (1) are to be expressed in electrical units]. From this it would follow that a pH-independent NFCP is an indication of a $(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r}$ value close to zero.

The fact that overlap in the regions of hydrogen and oxygen adsorption was observed in studying solutions in which the pH was high and the SO_4^{2-} concentration relatively low might have been a factor of significance in fixing the value of $(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r}$ and the pH-variation of the NFCP. In fact, let us rewrite the expression for $(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r}$ in the form $(\partial A_H/\partial\mu_{H^+})_{\varphi_r}/(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r}$. From [2, 14] it is known that $(\partial A_H/\partial\mu_{H^+})_{\varphi_r} < 0$, $(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r} > 0$ in the region of hydrogen adsorption. From this it would follow that $(\partial A_H/\partial\Gamma_{H^+})_{\varphi_r} < 0$ and $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0} > 0$, which is to say that an increase in the pH in the region of hydrogen adsorption should be accompanied by a displacement of the NFCP toward the negative side, just as reported in [2]. In the region of oxygen adsorption, Eq. (1) is to be replaced by

$$(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0} = \frac{(\partial A_0/\partial\Gamma_{H^+})_{\varphi_r}}{(\partial A_0/\partial\Gamma_{H^+})_{\varphi_r} + 1}, \tag{2}$$

A_0 being the concentration of adsorbed oxygen, expressed in electrical units. Since $(\partial A_0/\partial\mu_{H^+})_{\varphi_r} < 0$ and $(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r} > 0$, it follows that $(\partial A_0/\partial\Gamma_{H^+})_{\varphi_r} < 0$. When $|(\partial A_0/\partial\Gamma_{H^+})_{\varphi_r}| < 1$, $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0} < 0$, which is to say that there is the possibility of NFCP displacement in the positive direction with rising pH in the presence of adsorbed oxygen. In this sense, an overlap of the regions of hydrogen and oxygen adsorption could account for the failure of the NFCP to alter its position under a limited change in pH. Earlier measurements [2] were carried out with solutions which were more concentrated and more acidic than those used here, with the result that the NFCP always remained in the region of hydrogen adsorption.

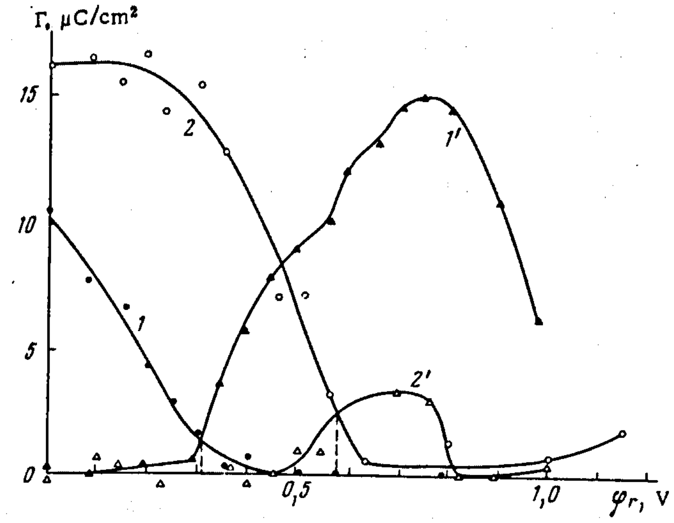

Fig. 2. Relation between the adsorption of cesium ions (1, 2) or sulfate ions (1', 2'), and the Pt/Pt electrode potential in $4 \cdot 10^{-3}$ N ($Cs_2SO_4 + H_2SO_4$) solutions with pH: 1, 1') 3.0; 2, 2') 6.0.

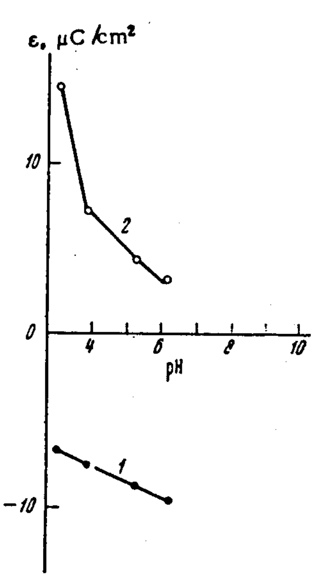

Fig. 3. Relation between surface charge and solution pH in $4 \cdot 10^{-3}$ N ($Na_2SO_4 + H_2SO_4$) solutions at $\varphi_r = 0$ (1) and at $\varphi_r = 0.7$ V (2).

The data obtained here were used to develop the relation between the potential and the surface charge at various values of the solution pH: $\varepsilon = \Gamma_{SO_4^{2-}} - \Gamma_{Na^+}$ (or Γ_{Cs^+}). The set of ε, φ_r curves was then used to develop the relation between ε and the pH (or φ) at φ_r=const; this was plotted, the slope of the resulting line measured, and the double layer capacitance at φ_r=const thereby determined. The results of these operations are shown in Fig. 3. The double layer capacitance at $\varphi_r = 0$ proved to be ~15 μF/cm² for Na_2SO_4 solutions, a value consistent with that obtained by potentiometric titration [15]. The double layer capacitance at $\varphi_r = 0.7$ V (100-30 μF/cm²) was higher than that calculated for $\varphi_r = 0$, and, in addition, pH-dependent. These observations could be explained by remembering that transistion had been made into the region of anion adsorption where the degree of surface coverage by oxygen would be pH-dependent. The data were also used to construct electrocapillary curves of the second type for various values of φ_r [16], construction being limited to a rather narrow φ interval, since the measurements had covered only the 3-6 pH range.

Our measurements at pH 6 showed the presence of two null free charge points for the Pt/Pt electrode. The second NFCP was that for the oxidized platinum electrode and was equal to ~0.47 V (with respect to the NHF) in $4 \cdot 10^{-3}$ N Na_2SO_4. The existence of a NFCP for the oxidized platinum electrode was also suggested by the measurements reported in [17, 18]. The value of this potential for 10^{-5} N H_2SO_4 is given as ~0.5 V (with respect to the NHF) in [17]. NFCP's in the region of oxygen adsorption have also been reported for ruthenium [19] and iridium [20]. The appearance of NFCP's for oxidized platinum at certain pH values could have been anticipated in view of the reported relation between potential and surface charge in acidic and alkaline solutions. In fact, increasing φ_r in acid solution causes a diminution in the negative surface charge, positive charging of the surface begins, with the positive charge, in turn, falling off as the value of φ_r is increased still further [2, 18, 21]. In an alkaline solution of inactive electrolyte, the platinum surface will be negatively charged at all values of φ_r [12, 18, 21]. There could clearly be intermediate pH values at which the ε, φ_r curve would cut the axis of abscissas twice. Special studies will be required for developing the pH-dependence of the NFCP of oxidized platinum.

We would like to thank Academician A. N. Frumkin for his interest in this work and for his valued remarks concerning it.

LITERATURE CITED

1. N. A. Balashova, N. T. Gorokhova, and M. I. Kulezneva, Élektrokhimiya, 4, 871 (1968).
2. O. A. Petrii, A. N. Frumkin, and Yu. G. Kotlov, Élektrokhimiya, 5, 476 (1969).
3. A. N. Frumkin and O. A. Petrii (Petry), Electrochim. Acta, 15, 391 (1970).
4. V. E. Kazarinov, Élektrokhimiya, 2, 1170 (1966); 8, 393 (1972).
5. O. A. Petrii, V. E. Kazarinov, and S. Ya. Vasina, Élektrokhimiya, 6, 729 (1970).
6. V. E. Kazarinov, O. A. Petrii, V. V. Topolev, and A. V. Losev, Élektrokhimiya, 7, 1365 (1971).

7. O. A. Petrii, V. E. Kazarinov, and I. G. Shchigorev, Élektrokhimiya, 6, 1565 (1970).
8. V. E. Kazarinov and N. A. Balashova, Dokl. Akad Nauk SSSR, 157, 1174 (1964).
9. V. E. Kazarinov and O. A. Petry (Petrii), J. Electroanalyt. Chem., 27, 1-2 (1970).
10. V. E. Kazarinov and O. A. Petrii, Élektrokhimiya, 8, 1731 (1972).
11. B. B. Damaskin, O. A. Petrii, and V. E. Kazarinov, Élektrokhimiya, 8, 1373 (1972).
12. V. F. Kazarinov, S. Ya. Vasina, O. A. Petrii, and V. V. Topolev, Élektrokhimiya, 9, 1123 (1973).
13. O. A. Petrii, A. N. Frumkin, and Yu. G. Kotlov, Élektrokhimiya, 4, 774 (1968); J. Res. Inst. Catalysis, Hokkaido Univ., 16, 367 (1968).
14. O. A. Petrii and Yu. G. Kotlov,, Élektrokhimiya, 6. 404 (1970).
15. R. Notoya, O. A. Petrii, S. Ya. Vasina, and A. N. Frumkin, Élektrokhimiya, 8, 904 (1972).
16. A. N. Frumkin and O. A. Petrii, Dokl. Akad. Nauk SSSR, 196, 1387 (1971).
17. N. A. Balashova and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 20, 449 (1938).
18. A. Shlygin, A. (N.) Frumkin and V. Medvedovsky, Acta Physicochim. URSS, 4, 911 (1936).
19. V. S. Entina and O. A. Petrii, Élektrokhimiya, 4, 457 (1968).
20. O. A. Petrii and Nugen van Tue, Élektrokhimiya, 6, 408 (1970).
21. A. N. Frumkin, A. I. Shlygin, Izv. Akad. Nauk SSSR, Ser. Khim., 773 (1936); Acta Physicochim. URSS, 5, 819 (1936).