ORIGINAL PAPER

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Influence of the specific adsorption of anions on the "double layer region" of the cyclic voltammetric curves obtained with platinized platinum electrodes

Abstract Cyclic voltammetric study of platinized electrodes restricted to the potential range corresponding to the "double-layer region" (350–700 mV on RHE scale) was carried out in acid medium in the presence of, HSO_4^-, $H_2PO_4^-$, Cl^- and ClO_4^- anions. It is shown that the shape of the voltammetric curves strongly depends on the nature of the anions present in the system. The phenomena observed are ascribed to the specific adsorption of anions. A correlation is found between the results of radiotracer adsorption studies (differential voltradiometric curves) and the voltammetric measurements.

Key words Platinized platinum · Cyclic voltammetry · Double-layer region · Anion-specific adsorption

Introduction

The cyclic voltammetric study of the behaviour of smooth polycrystalline and platinized electrodes in aqueous solutions has been the subject of several investigations during the last forty years [1–3].

Now it is a generally accepted view that, on the voltammetric curves obtained between the potentials corresponding to hydrogen and oxygen evolution, three main sections should be distinguished: (1) the hydrogen adsorption region (2) the double-layer region, and (3) the oxygen adsorption (or oxide) region.

The role of the anions in the behaviour of the hydrogen and oxygen adsorption region is discussed in detail in the literature and in text-books [1–3]; however, less attention is paid to the question how the double-layer region is influenced by various anions.

This question is mostly avoided owing to problems connected with the sensitivity of voltammetric measurements carried out in potential regions involving hydrogen or/and oxygen adsorption. For instance, the average pseudo-capacity in the hydrogen adsorption region could be ten times higher that the capacity in the double layer. Thus, in a voltammogram containing both hydrogen adsorption and double-layer regions, the current values registered in the double-layer region are ten times lower than those observed for the hydrogen region.

This means than in most cases changes in the double layer caused by the addition of anions cannot be observed, in contrast to the very pronounced effects observable in the hydrogen and oxygen adsorption regions.

Therefore, in order to get information on the role of anions in the voltammetric behaviour of platinized electrodes in the double-layer region, separate studies should be carried out restricting the potential cycling only to this region with a sensitivity which is at least one order of magnitude higher than that used in the cases where the hydrogen and double-layer regions are studied simultaneously.

It is hoped that by this approach the well-known differences in the specific adsorption of various anions on platinum could be well demonstrated by cyclic voltammetric measurements.

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Experimental

The voltammetric measurements were carried out in the cell that has been used for radiotracer adsorption studies for the last three decades (see, for instance, [4–5]). The geometric surface area of the main electrode, which forms the bottom of the cell, was 12.5 cm^2, and the roughness factor values characterizing the real surface area (obtained after platinization) were about 100 (determined from hydrogen adsorption). Owing to this situation, processes occurring with current densities of 10^{-2} μA cm^{-2} (referred to the real surface

area) could be followed easily in the cell used. ^{36}Cl-labelled Cl$^-$ ions (specific activity 26.7 mBq mmol^{-1}) were used for coupled volta-mmetric radiotracer adsorption studies. Potential values quoted are given on the RHE scale.

Considering the relatively high sensitivity of the voltammetric measurements and the small effects expected in the double-layer region, special attention was paid to the elimination of the possible role of organic impurities that could distort the voltammetric be-haviour of the systems studied. Therefore, in separate series of experiments the constancy of the voltammetric behaviour of each system was studied within the time scale of the anion effect studies.

Reproducibility of the voltammetric curves within this time scale was proof of the absence of any influence of any organic impurities.

(It will be shown later that cathodic and anodic voltammetric peaks ascribed to anion adsorption were symmetrical; the peak potentials were independent of the sweep rate, while the peak heights were proportional to it. These observations exclude any assumption concerning the possible role of organic impurities). In addition, effects specific to the nature of the anion can be observed only in cases where the role of organic impurities could be ne-glected.
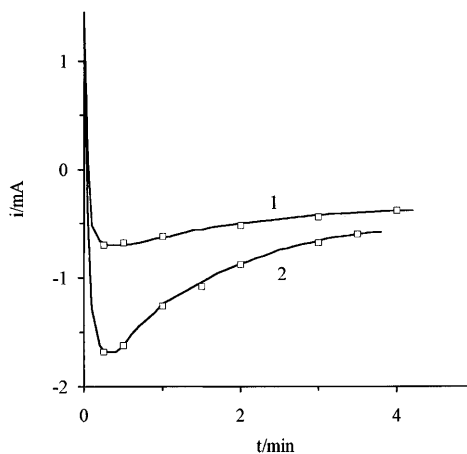
Results

In the first instance, a study of the influence of ClO$_4^-$, HSO$_4^-$ (SO$_4^{2-}$), Cl$^-$ and H$_2$PO$_4^-$ anions would seen ap-propriate, as these anions are mostly used in studies with platinized electrodes.
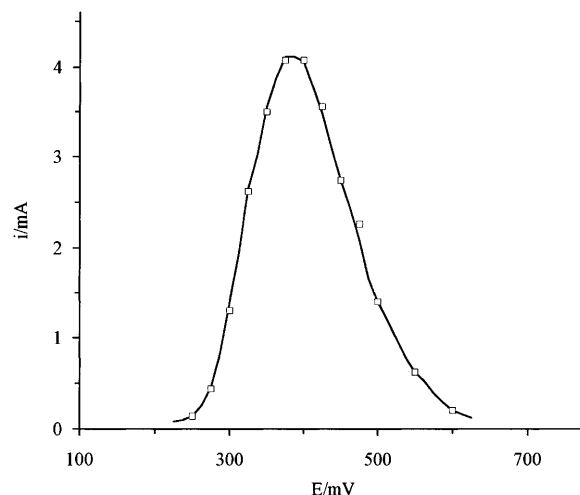
The study of the double-layer region in the presence of ClO$_4^-$ ions encounters significant difficulties due to the reduction of these ions at platinum electrodes, as dem-onstrated in a series of publications [6, 7].

The rate of the reduction process in 1 mol dm^{-3} HClO$_4$ solution is quite significant in the double-layer region, as demonstrated by potential switch experiments (Fig. 1), where current vs time curves obtained following potential switches from 0 to 500 and 550 mV, respec-tively, are shown.

The current vs time curves go through a minimum owing to the inhibition of the reduction process by the adsorption of Cl$^-$ ions formed in the reaction. (For a
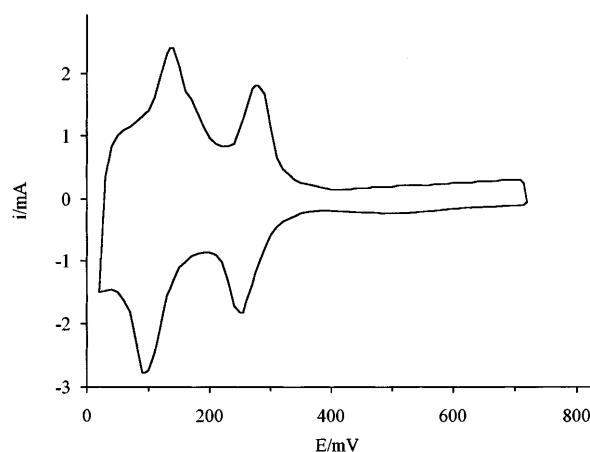

Fig. 2 Potential dependence of the minimum current obtained in experiments carried out according to those presented in Fig. 1

detailed discussion of these questions see previous communications [6, 7] and the literature cited therein.)

Plotting the minimum values against the final po-tential of the potential steps, the curve presented in Fig. 2 can be obtained. (The initial potential in each case is the same: 0 mV.) It may be seen from this figure that the reduction rate attains its maximum at a potential value situated inside the so-called double-layer region. These results were obtained in the presence of 1 mol dm^{-3} HClO$_4$ solution. On decreasing the HClO$_4$ con-centration the reduction rate decreases significantly; however, the possibility of the formation of reduction products, Cl$^-$ ions, which modify the surface by their adsorption cannot be completely excluded even at a very low concentration of ClO$_4^-$ ions. We return to this question later; however, it is evident that in the presence of ClO$_4^-$ ions we are not able to get strictly unambiguous results characterizing the behaviour of the double-layer region. In the case of H$_2$SO$_4$, more reliable results are to be expected. Figure 3 shows a voltammetric curve ob-

Fig. 1 Current vs time curves following potential switches from 0 mV in 1 mol dm^{-3} HClO$_4$ to 550 mV (1) and 500 mV (2)

Fig. 3 Voltammetric curve in the presence of 1 mol dm^{-3} H$_2$SO$_4$

Fig. 4 Voltammetric curves at three different sweep rates in the potential range corresponding to the double-layer region in the voltammogram presented in Fig. 3
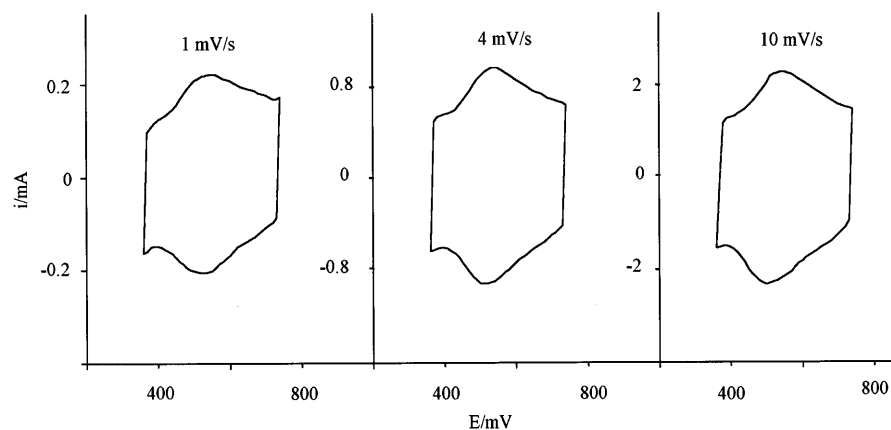
tained in 1 mol dm^{-3} H$_2$SO$_4$ involving both the hydrogen and double-layer regions. In this presentation no characteristic features in the double-layer region can be observed. However, studying only the double-layer region at various sweep rates, the curves presented in Fig. 4 are obtained.

The main conclusions to be drawn from this figure are as follows:

1. Well-defined peaks appear on both cathodic and anodic sweeps.
2. These peaks are symmetrical.
3. The position of the peaks does not depend on the sweep rate.
4. The height of the peaks is proportional to the sweep rate.

All this means that the peaks correspond to surface phenomena, presumably adsorption of the anions. It is known from the literature (and from our previous radiotracer studies [4–9]) that the adsorption strength of the H$_2$PO$_4^-$ ion is higher than that of HSO$_4^-$ ions. Thus, in the case of the validity of the above assumption, a change in the double-layer behaviour can be expected following the addition of H$_3$PO$_4$ to the system. This actually happens, as shown in Fig. 5. On the other hand, the adsorption strength of Cl$^-$ ions on platinum is significantly higher than that of HSO$_4^-$ or H$_2$PO$_4^-$ ions. Cl$^-$ ions displace adsorbed HSO$_4^-$ even at very low $c_{Cl^-}/c_{HSO_4^-}$ concentration ratios in the solution phase. (This effect was clearly demonstrated by radiotracer adsorption studies [4].) Figure 6 shows the effect of Cl$^-$ ions on the voltammetric behaviour in the double-layer region observed in the presence of 1 mol dm^{-3} H$_2$SO$_4$.

This figure demonstrates that the peaks at about 500 mV, characteristic for the HSO$_4^-$ species, completely disappear, and a new peak-like section appears on the anodic sweep at significantly lower potentials. It can be assumed that the adsorbed HSO$_4^-$ species are completely displaced by Cl$^-$ ions and the surface is occupied by Cl$^-$ ions alone.

This assumption is confirmed by a coupled voltammetric and radiotracer adsorption study using ^{36}Cl-labelled Cl$^-$ ions present in low concentration in 1 mol
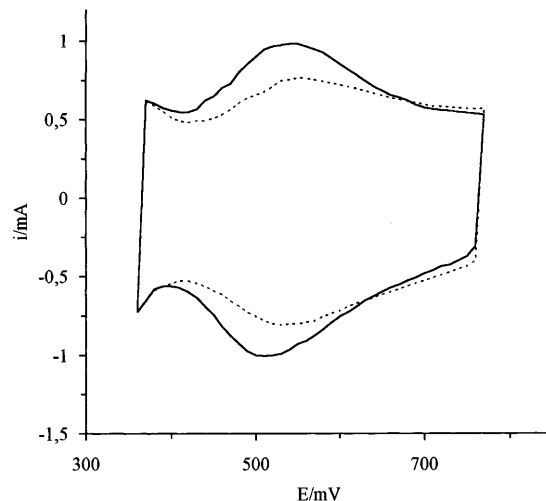
Fig. 5 Effect of H$_3$PO$_4$ on the voltammetric behaviour of a platinized electrode in the double-layer region: (.....) 1 mol dm^{-3} H$_2$SO$_4$; (——) after addition of 1×10^{-1} mol dm^{-3} H$_3$PO$_4$; sweep rate 4 mV s^{-1}
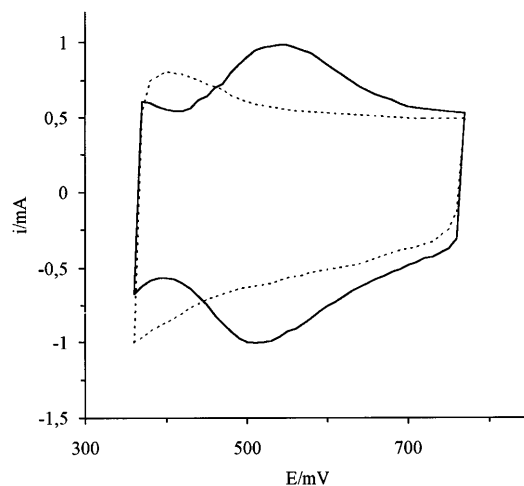
Fig. 6 Effect of Cl$^-$ ions on the voltammetric behaviour of a platinized electrode in the double-layer region: (——) 1 mol dm^{-3} H$_2$SO$_4$; (.....) after addition of 2×10^{-2} mol dm^{-3} HCl; sweep rate 4 mV s^{-1}
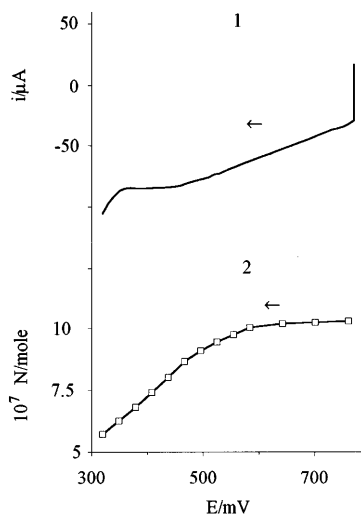
Fig. 7 Simultaneous voltammetric (*1*) and radiotracer desorption (voltradiometric) study of Cl^- ions (*2*) present in 1×10^{-4} mol dm^{-3} concentration in 1 mol dm^{-3} H_2SO_4; sweep rate 0.6 mV s^{-1}

dm^{-3} H_2SO_4 supporting electrolyte. The desorption of Cl^- ions during a cathodic sweep with a 0.6-mV s^{-1} sweep rate starting from 750 mV is shown in Fig. 7.

The negative potential shift and the corresponding charge transfer are coupled with the simultaneous desorption of Cl^- ions. The charge corresponding to the change in the amount of adsorbed Cl^- ions and the charge involved in the cathodic sweep are not far from each other. This may be seen Fig. 8, where a rough proportionality between these two quantities can be observed. However, owing to the presence of the great excess of HSO_4^- ions, any further calculation would be misleading.

An attempt is made to study the voltammetric behaviour in the presence of ClO_4^- ions. In order to minimize the role of the ClO_4^- reduction, 1×10^{-1} mol dm^{-3} $HClO_4$ solution and relatively high sweep rates (4 mV s^{-1}) were used.

In accordance with expectations (relatively low adsorbability of the ClO_4^- species), the shape of the voltammetric curve obtained for ClO_4^- ions differs significantly from that of other anions (dotted line in
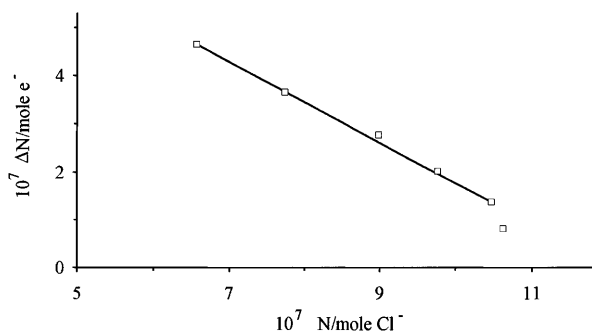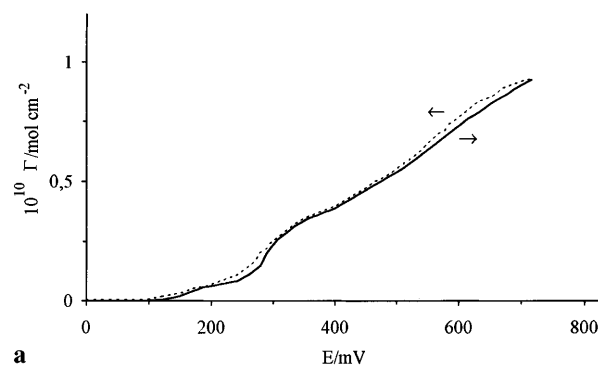

Fig. 8 Relationship between the charge involved ΔN (expressed in amount of electrons) and Cl^- adsorption during the coupled voltammetric and voltradiometric study presented in Fig. 7
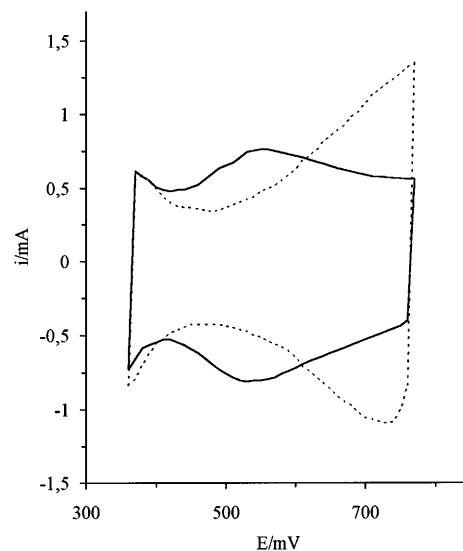

Fig. 9 Voltammetric curve obtained in the presence of 1×10^{-1} mol dm^{-3} $HClO_4$ (*dotted line*) and following the addition of 5×10^{-2} mol dm^{-3} H_2SO_4 (*full line*); sweep rate 4 mV s^{-1}

Fig. 9). Addition of H_2SO_4 in 5×10^{-2} mol dm^{-3} concentration (full line) completely restores the behaviour observed for HSO_4^- ions. It is of interest that the sections above 500–550 mV observed in the presence of ClO_4^-

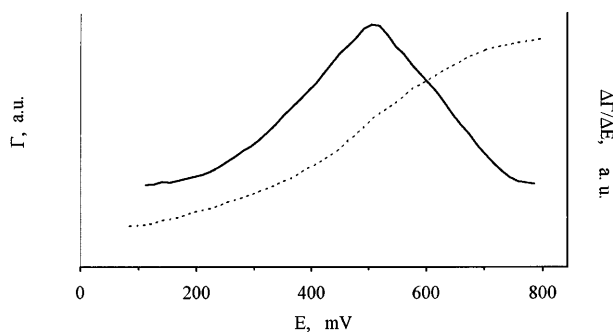
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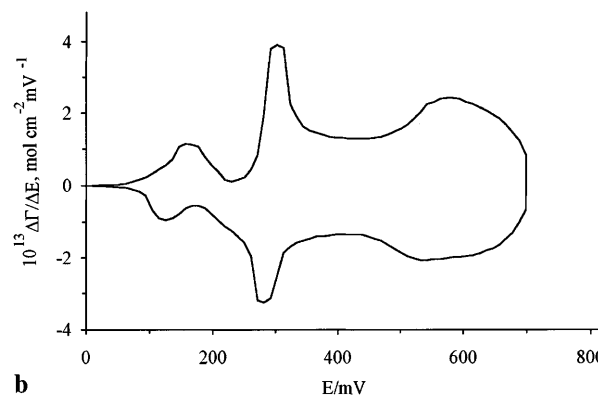
b

Fig. 10 A Cyclic voltradiometric curve for the adsorption of labelled HSO_4^- ions ($c = 1.7 \times 10^{-3}$ mol dm^{-3}) in 1 mol dm^{-3} $HClO_4$; sweep rate 0.25 mV s^{-1}. **B** The differential voltradiometric curve corresponding to Fig. 11A

Fig. 11 Schematic representation of the potential dependence of the adsorption (Γ) of $H_2PO_4^-$ ions (*dotted line*, in arbitrary units) and the corresponding $\Delta\Gamma/\Delta E$ vs E curve (*full line*, in arbitrary units). (Data from [9])

Fig. 12 Comparison of the $\Delta\Gamma/\Delta E$ vs E (*full line*) curve (in Fig. 12) with the anodic section of the cyclic voltammetric (*dotted line*) curve (in Fig. 5) for H_3PO_4

ions (and the absence of other anions) is completely eliminated by the addition of HSO_4^- (SO_4^{2-}) ions.

The occurrence of the section under consideration can be explained not only in terms of ClO_4^- adsorption but in terms of OH or O adsorption as well. It is possible that both alternatives play some role. (The specific adsorption of HSO_4^- species could inhibit both processes equally.)
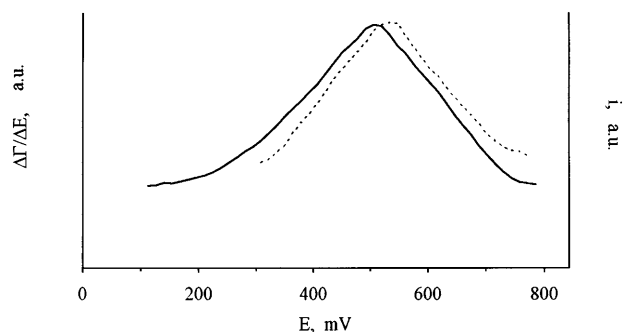
Discussion

The results of previous radiotracer adsorption studies [4, 8–10] carried out with platinized electrodes furnished clear evidence that there is a significant change in the extent of the specific adsorption of anions on platinum in the potential range corresponding to the double-layer region. Some of these results are presented in Figs. 10 and 11.

The parallel between the voltammetric and the volt-radiometric behaviour in the double-layer region was shown in the case of Cl^- ions (see Figs. 7 and 8).

The shapes of $\Delta\Gamma/\Delta E$ vs E functions presented in Fig. 10 and Fig. 11 for $H_2PO_4^-$ and HSO_4^- ions respectively are very similar to the corresponding sections on the voltammetric curves presented in Figs. 4 and 5 respectively.

Thus, Fig. 12 shows that, in the case of HSO_4^- ions, by appropriate transformation the $\Delta\Gamma/\Delta E$ vs E and the voltammetric curves could be well fitted to each other. (Similar coincidence can be observed for $H_2PO_4^-$ ions.)

This very fact confirms the assumption that the voltammetric behaviour of a Pt electrode in the double-layer region is strongly influenced by the specific adsorption of anions. Thus, a detailed study of this section in the presence of various anions could furnish information about specific anion adsorption.

References

1. Christensen PA, Hamnett A (1994) Techniques and Mechanisms in Electrochemistry, Blackie Academic Professional, London, p 228
2. Koryta J, Dvoøák J, Kavan L (1993) Principles of electrochemistry. Wiley, NewYork, p 352
3. Sawyer DT, Sobkowiak A, Roberts JL Jr (1995) Electrochemistry for chemists. Wiley, NewYork, p 216
4. Horányi G (1980) Electrochim Acta 25: 43
5. Horányi G (1995) Rev Anal Chem 14: 11
6. Horányi G, Bakos I (1992) J Electroanal Chem 331: 727
7. Bakos I, Horányi G (1993) J Electroanal Chem 347: 383
8. Horányi G, Inzelt G (1978) J Electroanal Chem 86: 215
9. Horányi G, Rizmayer EM, Inzelt G (1978) J Electroanal Chem 93: 183
10. Horányi G, Rizmayer EM (1987) J Electroanal Chem 218: 337