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INFLUENCE OF ADSORPTION OF METHANOL ON THE KINETIC BEHAVIOUR OF ADSORBED HYDROGEN AND THE DOUBLE LAYER CAPACITY ON PLATINUM

By

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Abstract

The influence of methanol in electrolyte on the exchange current of the discharge-ionization reaction of hydrogen and the pseudocapacity of the platinum hydrogen electrode was determined by the method of impedance measurements at potentials of the hydrogen region.

It was found that the pseudocapacity and the exchange current were sharply decreased by the adsorption of methanol on the electrode surface and the influence of methanol was observed mainly on the strongly chemisorbed hydrogen.

The influence of methanol on the capacity of the electric double layer was also observed.

Introduction

It is known that the adsorption of organic substances has a strong influence on the structure of the electric double layer and the rate of electrochemical reaction at the electrode-solution interface¹⁾. These phenomena have been investigated in detail mainly on the mercury electrode. At the present time the investigation of the influence of organic substances on the electrode processes on platinum is a matter of great interest for the fuel cell problem.

BREITER^{2,3)} has shown that the double layer capacity of the platinum electrode decreases in the presence of methyl and amyl alcohols. It also follows from his data that the exchange current of the discharge-ionization reaction of hydrogen decreases in the presence of organic substances. This result is not surprising, because a part of the surface is occupied by adsorbed particles of the type $\text{HCO}^{1)}$ in the case of adsorption, for example, of

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methanol and hydrogen is not adsorbed on these sites. Therefore, it is an interesting problem whether the decrease of the exchange current of the reaction described above can be ascribed simply to the occupation of the adsorption sites or to other factors pointed out in the literature¹⁾, for example, to the change of the bond energy of H_{ads} on the sites adjacent to those occupied with adsorbed organic substances.

In order to solve this question, we used the method of impedance measurements which was developed in the works of DOLIN and ERSHLER⁴⁾ for the quantitative investigation of the kinetics of the discharge-ionization of hydrogen. The information on the influence of methanol on the electric double layer capacity was also obtained by means of this method.

Experimental part

The cell and method used in the present work were the same as described previously⁵⁾. The test electrode made of platinum wire of diameter $50\ \mu$ and length 3.5 mm was located at the center of a platinum cylinder which worked as a counter electrode.

Measurements were carried out by means of a high frequency vector-polarograph which was designed by I. E. BRYKSIN. Using this instrument, it is possible to determine the ohmic and capacitive components of the impedance of an equivalent circuit in a parallel combination in the course of a linear change of the electrode potential. These measurements were carried out with an alternating current in the range of the frequency ω from 40 to 5000 Hz at the amplitude of the potential 5 mV. The sweep rate of the electrode potential was set up at 7 mV/sec.

The electrode was treated preliminarily for a long time by cyclic polarization in the potential range $\varphi_r = 0.05 \sim 1.5$ V (referred to the reversible hydrogen electrode in the same solution) until the reproducible phenomena were obtained.

The values of the capacity and resistance of the equivalent circuit of DOLIN-ERSHLER⁴⁻⁶⁾ were evaluated in the following from the values of the capacity C_p and resistance R_p obtained in the results of the measurements.

The resistance measured at frequency 100 kHz by an equivalent circuit of series combination at $\varphi_r = 500$ mV was taken as the solution resistance as described below.

The measurements of the impedance at frequencies higher than 5 kHz were carried out by means of an impedance bridge combined with a potentiostat⁵⁾. This arrangement enables us to measure the capacity and resistance of an equivalent circuit in a series combination in the frequency range

20 Hz~100 kHz, and has a programming attachment which gives a possibility to polarize the electrode periodically with anodic-cathodic impulses. This treatment of the electrode by the periodic impulses makes it possible to get the reproducible condition of the electrode.

Special attention was paid to the purification of the chemical agents used in the present work. Methanol of the chemically pure grade was distilled two times. The base electrolyte solutions were preliminarily purified by a platinum net in the hydrogen atmosphere.

The data were referred in calculation to true unit area of the electrode which was determined by the quantity of adsorbed hydrogen at $\varphi_r = 0$ by the standard method⁷⁾.

Results and Discussion

1. The adsorption pseudocapacity of the platinum electrode and the exchange current of the discharge-ionization reaction.

Figures 1 and 2 show the experimental results of the potential dependence of the capacity C_p and the reciprocal resistance $1/R_p$ at various frequencies in 1N H_2SO_4 solution. The components in the equivalent circuit of DOLIN-ERSHLER, *i.e.*, the reaction resistance of the discharge-ionization of hydrogen r and the adsorption pseudocapacity C_{ads} were calculated from these data.

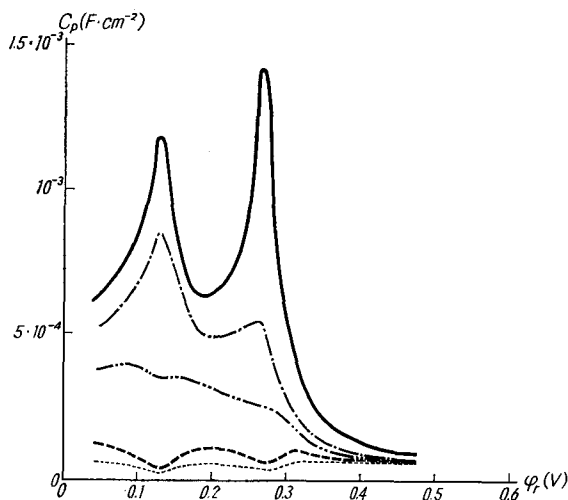


Fig. 1. Dependence of C_p on φ_r in 1N $H_2SO_{4(aq)}$ at various frequencies; 40 Hz (—), 600 Hz (— · — ·), 1200 Hz (— · · —), 2500 Hz (· · · · ·) and 5000 Hz (· · · · ·).

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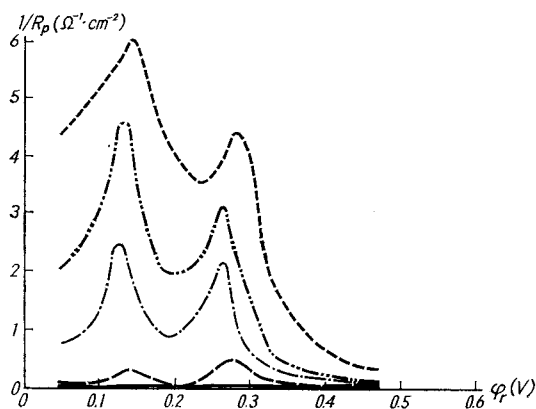


Fig. 2. Dependence of R_p on φ_r in 1N $H_2SO_{4(aq.)}$ at various frequencies; 40 Hz (—), 160 Hz (---), 600 Hz (- · - · -), 1200 Hz (- · · -) and 2500 Hz (- - - - -).

From the value of $1/r$ the exchange current of the discharge-ionization reaction of hydrogen i_0 was calculated⁴⁻⁶⁾. The results of the calculation C_{ads} and i_0 were shown in Fig. 3 and 4. The data thus obtained show that C_{ads} and i_0 go through two maxima at 135 and 270 mV and these maxima can be related to the presence of two states of the adsorbed hydrogen on platinum⁸⁾.

It should be noted that the values of C_{ads} calculated from data obtained at different frequencies of the alternating current coincide satisfactorily with

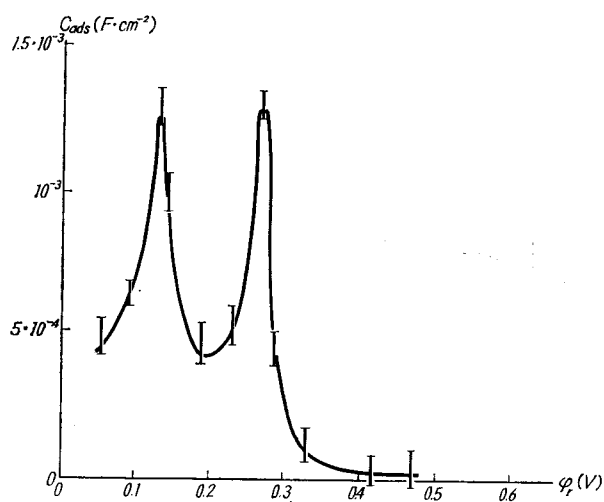


Fig. 3. Dependence of C_{ads} on φ_r in 1N $H_2SO_{4(aq.)}$ at various frequencies.

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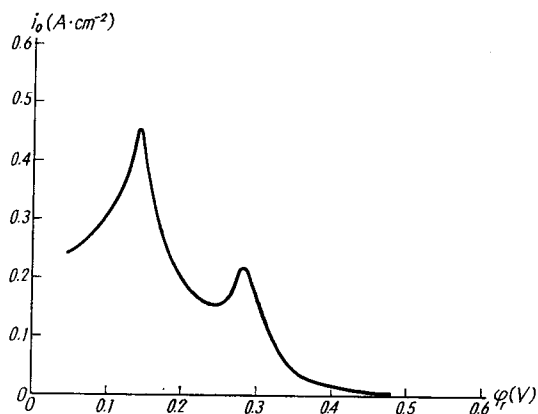


Fig. 4. Dependence of i_0 on φ_r in 1N $\text{H}_2\text{SO}_{4\text{aq.}}$ at frequency 2400 Hz.

each other. However, the values of i_0 are markedly different. This can be explained by the fact that the equivalent circuit of DOLIN-ERSHLER holds for the platinum hydrogen electrode only approximately. For comparison, the data obtained at the frequency 2400 Hz were used in what follows. The reasons for the dispersion of the capacity and resistance were discussed in the work⁴), in which it was shown that at $\omega \rightarrow 0$, $C_p = C_{\text{ads}} + C_d$, but at $\omega \rightarrow \infty$, $1/R_p = 1/r$.

Figures 5~8 show the relations $C_p - \varphi_r$, $1/R_p - \varphi_r$, $C_{\text{ads}} - \varphi_r$ and $i_0 - \varphi_r$ in

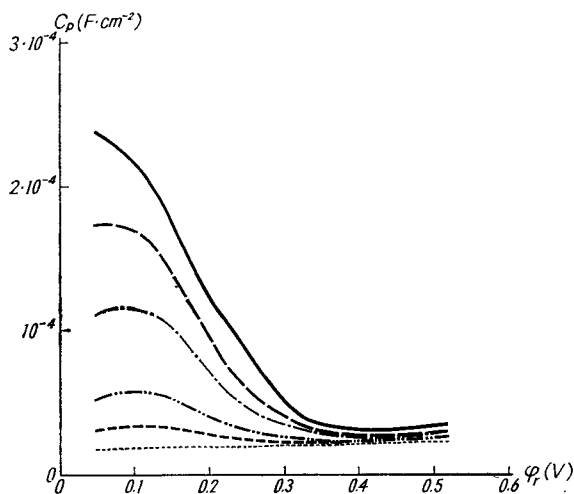


Fig. 5. Dependence of C_p on φ_r in 1N $\text{H}_2\text{SO}_{4\text{aq.}}$ + 0.5 M CH_3OH at various frequencies; 40 Hz (—), 160 Hz (---), 600 Hz (- · - ·), 1200 Hz (- · · - · ·), 2500 Hz (.....) and 5000 Hz (.....).

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1N H₂SO₄ + 0.5 M CH₃OH solution. The measurements were carried out in the range of the periodic change of the platinum electrode potential 0.05~1.4 V. Only a part of the curves concerned with the hydrogen and double layer potential regions on the platinum electrode are shown in these Figures. It follows from Fig. 7 that the value of C_{ads} in the presence of methanol

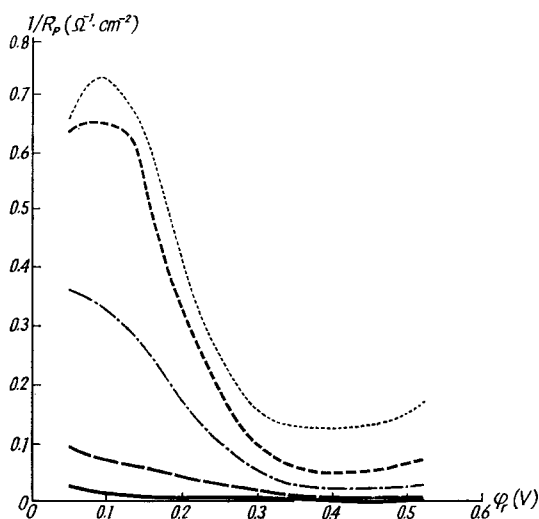


Fig. 6. Dependence of R_p on φ_r in 1N H₂SO_{4aq.} + 0.5 M CH₃OH at various frequencies; 40 Hz (—), 160 Hz (---), 600 Hz (- · - ·), 2500 Hz (- - - -) and 5000 Hz (·····).

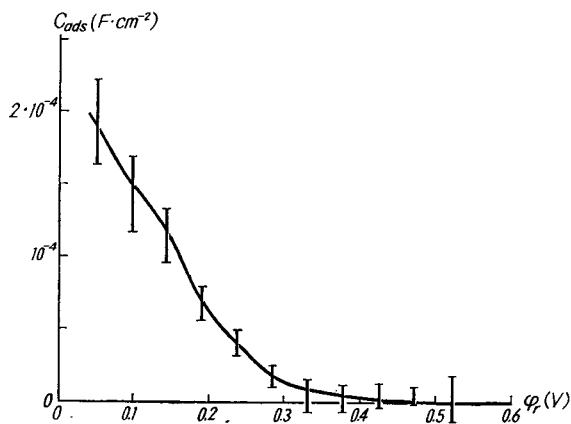


Fig. 7. Dependence of C_{ads} on φ_r in 1N H₂SO_{4aq.} + 0.5 M CH₃OH at various frequencies.

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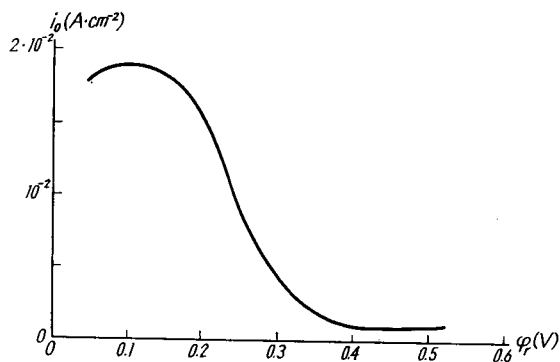


Fig. 8. Dependence of i_0 on φ_r in 1N $H_2SO_{4aq.}$ + 0.5 M CH_3OH at the frequency 2400 Hz.

calculated from the data obtained at different frequencies also remains unchanged independent of the frequency. On the other hand, the values i_0 are strongly different, *i.e.* the value of i_0 increases with the increase of frequency.

It can be seen from the data obtained that the adsorption pseudocapacity curve changes its shape sharply in the presence of adsorbed methanol. The maximum is not observed now on this curve, but a monotonous decrease of the capacity can be seen with the displacement of the potential to the anodic side, and furthermore the values of the capacity are sharply decreased. These phenomena can be related to the adsorption of methanol.

The dependence of the exchange current of the discharge-ionization

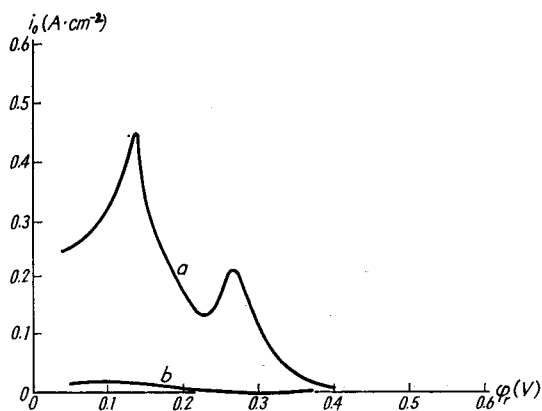


Fig. 9. Dependence of i_0 on φ_r ; (a) in 1N $H_2SO_{4aq.}$, (b) in 1N $H_2SO_{4aq.}$ + 0.5 M CH_3OH .

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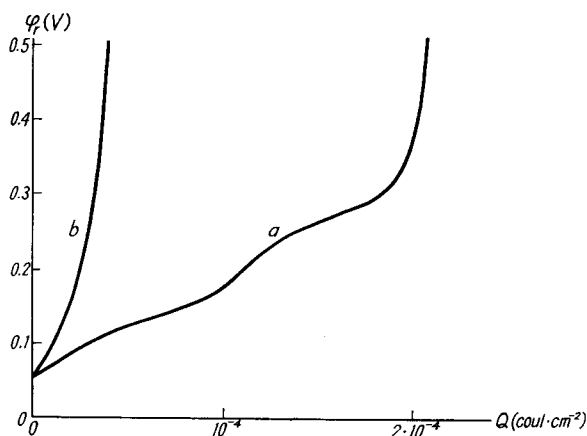


Fig. 10. Relation φ_r and Q ; (a) in 1N $\text{H}_2\text{SO}_{4\text{aq.}}$,
(b) in 1N $\text{H}_2\text{SO}_{4\text{aq.}}$ + 0.5 M CH_3OH .

reaction of hydrogen on potential are shown in Fig. 9, from which it can be seen that methanol has a great influence on the exchange current of the reaction studied. In the presence of methanol the exchange current is practically close to zero at $\varphi_r > 0.3$ V. Thus, it can be seen that the primary influence of methanol on the exchange current is observed for strongly bound hydrogen.

The charging curves of the platinum electrode were obtained by the integration of $C_{\text{ads}} - \varphi_r$ curves measured at the least frequency (40 Hz) which were presented in Fig. 10. The decrease of the quantity of adsorbed hydrogen at a given value of φ_r in the presence of methanol can readily be estimated from these curves and compared with the decrease of the exchange current. The calculation shows that the exchange current decreases more strongly than the decrease of the surface coverage. This result and the primary influence of methanol on the exchange current of strongly bound hydrogen also can probably be explained by the influence of methanol on the bond energy of adsorbed hydrogen¹⁾.

It follows from the results of measurements in solutions with addition of methanol that no other oxidation-reduction system except $\text{H}_{\text{ads}} \rightleftharpoons e^- + \text{H}^+$ is observed in the presence of methanol. This result verifies the conclusion that the potential established on platinum in the presence of organic substances is determined by the reaction of the discharge-ionization of hydrogen⁹⁾.

2. The capacity of electric double layer in the presence of methanol

For the measurement of the capacity of the electric double layer, solu-

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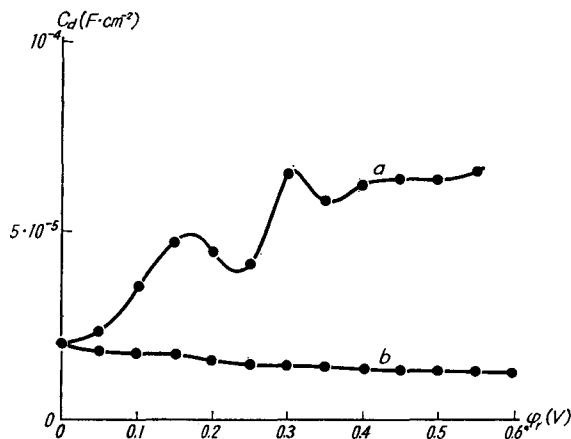


Fig. 11. Dependence of C_d on φ_r ; (a) in $10^{-2}N$ $H_2SO_{4aq.}$ + $1N$ $Na_2SO_{4aq.}$, (b) in $10^{-2}N$ $H_2SO_{4aq.}$ + $1N$ $Na_2SO_{4aq.}$ + 0.5 M CH_3OH .

tions $10^{-2}N$ H_2SO_4 + $1N$ Na_2SO_4 were used. In these solutions the exchange current is strongly decreased as compared with that in solution $1N$ H_2SO_4 ⁶⁾ because of comparatively low concentration of hydrogen ion and addition of Na_2SO_4 in large quantity. Therefore it becomes possible to obtain the dependence of the capacity of the double layer on the electrode potential in the whole range of the potential at frequencies $20 \sim 100$ kHz.

Figure 11 shows the curves of the double layer capacity obtained in the solutions described above and in the solution of the same composition but including 0.5 M CH_3OH . In the measurement of the latter curve the electrode potential was preliminarily changed linearly with time in the range $0 \sim 1.4$ V in the solution studied. Then after returning to $\varphi_r = 0$, the measurements of the capacity were carried out.

In the base electrolyte solution the amount of the capacity is approximately $60 \mu F/cm^2$ in the potential region of the sulfate ion adsorption on platinum. When the electrode potential approaches to the reversible hydrogen potential, maxima are observed on the capacity curve which potentials correspond to those at the maxima on the $C_{ads} - \varphi_r$ curves. The nature of these maxima on the curves of the double layer capacity is not clear. The capacity decreases sharply at $\varphi_r < 0.15$ V. This can probably be related to the transition to the region of the adsorption of cation and to the occupation of the platinum with adsorbed hydrogen which reduces the double layer capacity¹⁰⁾.

In the presence of methanol the capacity decreases at $\varphi_r > 0$ V as observed usually in the case of adsorption of organic substances. However, the values

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of the capacity are found to be nearly the same at $\varphi_r=0$ both in the cases of absence and presence of methanol. Another interesting feature consists in the fact that the double layer capacity increases with the decrease of φ_r , even though the surface coverage with organic substances remains constant under the experimental conditions. When methanol is adsorbed, the displacement of adsorbed hydrogen occurs which would result in the increase of the capacity. However, methanol itself also decreases the capacity. It is obvious that the compensation may take place between the effects caused by the decrease of the adsorption of hydrogen and by the adsorption of methanol in certain conditions. In the present case this takes place at $\varphi_r=0$ V. The similar conclusion was deduced in the work¹¹⁾.

Acknowledgements

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