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Hydrogen Overvoltage on Nickel in Solutions of Acids

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Lukowzew, Lewina and Frumkin[1], while investigating the overvoltage on nickel, arrived at the conclusion that depending on the pH of the solution different mechanisms may take place. Thus, in acid solutions the theory of slow discharge of hydrogen ions proved valid, and in alkaline solutions, of hydrogen entering into the molecule of water.

The object of the present investigation was a study of the overvoltage mechanism on nickel electrodes in acid solutions for a wide range of concentrations, since in the paper cited this range was limited, as well as the elucidation of the dependence of overvoltage on the nature of anions and on the structure of the double layer.

Experimental

In the treatment of nickel and preparation of solutions particular attention was paid to their purification. The presence of impurities accounts for the discrepancy of the results in the majority of papers devoted to the overvoltage on nickel. The hydrochloric acid was prepared by solution of gaseous HCl in twice distilled water. The HBr solutions were prepared from chemically pure concentrated hydrobromic acid distilled in a hydrogen atmosphere. The middle fraction of the constant-boiling mixture was kept in a sealed ampoule and when necessary used for preparing solutions of the desired concentration. Purification of sulphuric acid solutions was

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[1] P. Lukowzew, S. Lewina and A. Frumkin, Acta Physicochimica URSS, 11, 21 (1939).

carried out only by prolonged electrolysis in a hydrogen atmosphere. To prepare the solutions chemically pure Kahlbaum acid (*"mit Garantieschein"*) was used. The HCl solutions in ethyl alcohol were prepared by the method described in the paper of Lewina and Silberfarb[2].

The nickel cathode (a plate of Kahlbaum nickel, 15 cm.^{2} in size) was washed with hot KOH solution, then with water and, finally, before the experiment, heated at 420—450° C in a hydrogen atmosphere to remove the surface oxides.

In the present investigation the method of overvoltage measure ment was analogous in substance to that described by Lukowzew, Lewina and Frumkin[1]. In contradistinction to the latter the heating of the cathode in a hydrogen atmosphere was conducted without raising the electrode; this simplified the design of the whole apparatus and its operation to a considerable extent. Moreover, the arrangement of the apparatus was modified in such a way that the platinized platinum cathode serving for the preliminary purification of solutions by electrolysis, was used as the anode in polarization measurements; the latter modification also simplified the design of the apparatus.

Experimental results and their discussion

In accordance with the aim of the present work, in the first place the overvoltage in HCl solutions was studied over a concentration range from $1\,N$ to $5 \times 10^{-5}\,N$ at current densities from 1×10^{-8} A/cm.^{2} to 1×10^{-2} A/cm.^{2}.

The results of these measurements are given in Fig. 1.

The $\eta - \lg i$ curves have the same character as in the work of Bowden and Rideal[3], as well as in that of Lukowzew, Lewina and Frumkin. At very low current densities the overvoltage practically does not change with an increase of current density and the $\eta - \lg i$ curve in this region is almost horizontal. At higher current densities, between the overvoltage and the logarithm of current

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[2] S. Lewina u. M. Silberfarb, Acta Physicochimica URSS, **4**, 275 (1936).

[3] F. Bowden and E. Rideal, Proc. Roy. Soc. London, **A 120**, 86 (1928).

density there exists a linear relation. The curves follow **Tafel's** equation $\eta = a + b \lg i$ with the coefficient b equal to 0.093—0.103. The more concentrated the solution the greater the value of b; thus, *e. g.*, in 0.0015 N HCl, $b = 0.093$; and in 1 N HCl, $b = 0.103$. In 0.0015 N HCl and more dilute solutions the $\eta - \lg i$ curves coincide,

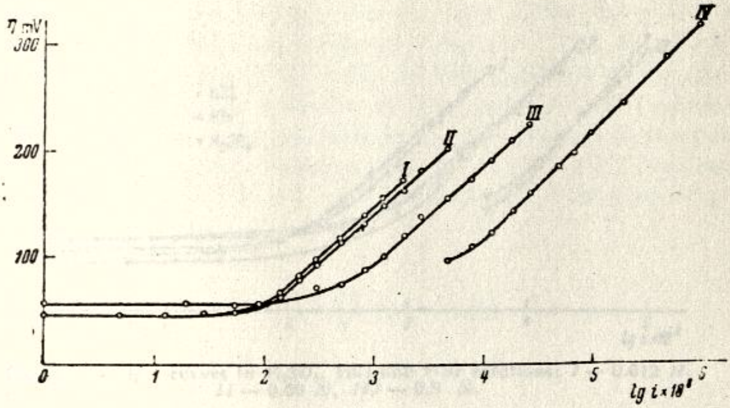

Fig. 1. $\eta - \lg i$ curves in HCl solutions : I — 0.0015 N, II — 0.012 N, III — 0.085 N, IV — 0.90 N.

i. e., the overvoltage does not vary with concentration. At concentrations from 0.01 N to 1 N the overvoltage increases by about 58 mV with a tenfold dilution. The difference of overvoltage in 0.012 N and 0.0015 N solutions is 11 mV.

In Fig. 2 are shown the experimental results in solutions of H_2SO_4, HCl and HBr at different concentrations. As seen from the diagram, the $\eta - \lg i$ curves in different acids at equal concentrations practically coincide. The curves for H_2SO_4 are somewhat steeper as compared with the curves for HCl and HBr.

To elucidate the relation between the double layer structure and the overvoltage, the influence of neutral salts was studied. To the solutions of H_2SO_4, HCl, HBr, respectively $La_2(SO_4)_3$, $LaCl_3$ and $LaBr_3$ were added. As will be seen from Fig. 3, in the upper part of the curves an increase of overvoltage is observed, which is the stronger the more dilute the solution; in the initial part the addition of salts causes a lowering of overvoltage. The curves for the pure acids and for the same acids with salt addition intersect (see Fig. 3).

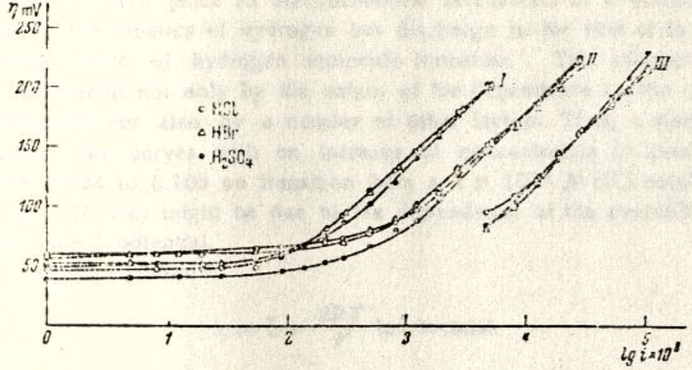

Fig. 2. η — lg i curves in H_2SO_4, HCl and HBr solutions: I — 0.012 N, II — 0.09 N, III — 0.9 N.

The curves obtained with different acids after salt addition, like those for the solutions of pure acids, H_2SO_4, HCl and HBr, practically coincide with each other.

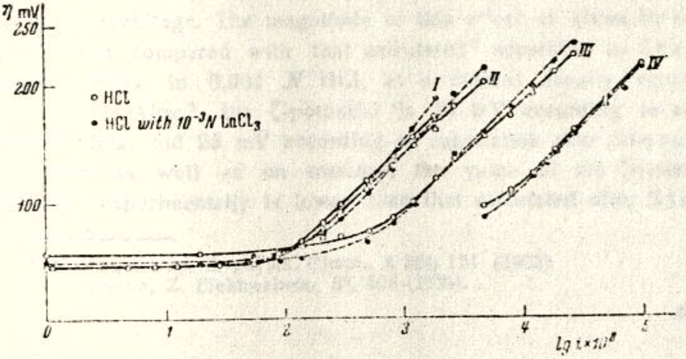

Fig. 3. Effect of $LaCl_3$ addition on overvoltage in HCl solutions: I — 0.0015 N HCl, II — 0.012 N HCl, III — 0.085 N HCl, IV — 0.90 N HCl.

When analysing the experimental data obtained, the following conclusions may be made. The overvoltage on nickel in acids cannot evidently be accounted for by a single mechanism over a wide range of concentrations.

In the concentration range from 0.01 N to 1 N, where upon a tenfold dilution the overvoltage increases by about 58 mV, there probably takes place an electrochemical mechanism of overvoltage due to the kinetics of hydrogen ion discharge in the first or in the second stage of hydrogen molecule formation[1]. This assumption is evidenced not only by the nature of the dependence on the concentration but also by a number of other factors. Thus, a steeper rise of the curves with an increase of concentration (b changes from 0.093 to 0.103 on transition from a 1×10^{-3} N HCl solution to a 1 N one) might be due to the dependence of the overvoltage upon the ζ-potential.

From equation[4]

$$\eta = \zeta + \frac{2RT}{F} \ln i + \text{const.}$$

we have

$$\frac{\partial \eta}{\partial \ln i} = \frac{\partial \zeta}{\partial \ln i} + \frac{2RT}{F},$$

where $\frac{\partial \zeta}{\partial \ln i} < 0$ and, hence, the coefficient b is smaller than $2.3\frac{2RT}{F}$. With an increase in concentration this correction is reduced and the value of b tends to $2.3\frac{2RT}{F}$. The increase of overvoltage in the presence of neutral salts also proves the effect of the ζ-potential on overvoltage. The magnitude of this effect as given by experiment was compared with that calculated[4] according to **Stern's** theory[5]. Thus, in 0.001 N HCl, at a current density equal to 1.39×10^{-5} A/cm.^{2}, the ζ-potential is 14 mV according to experimental data, and 25 mV according to calculation after **Stern**.

Here, as well as on mercury, the value of the ζ-potential obtained experimentally is lower than that calculated after **Stern**.

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[4] A. Frumkin, Z. physik. Chem., A 164, 121 (1933).
[5] O. Stern, Z. Elektrochem., 30, 508 (1924).

This discrepancy was discussed in detail in the paper of Lewina and Sarinsky[6].

Thus, for a range of concentrations from 0.01 N to 1 N, an electrochemical mechanism of overvoltage is evidenced both by the concentration dependence and the increase of the coefficient b with increase of concentration, as well as by the change of overvoltage in the presence of neutral salts. All these phenomena cannot be explained by the recombination theory.

Recently Horiuti, Okamoto and Hirota[7], using the method of the transition state, gave a new theoretical foundation to the recombination theory. According to these authors, when the current density reaches 1×10^{-5} A/cm.^{2} there should be a "saturation current", and the $\eta - \lg i$ curve should sharply rise. As shown by Fig. 1, even at a current density exceeding this value 1000 times, namely 1×10^{-2} A/cm.^{2}, the $\eta - \lg i$ curve retains a normal linear course, and no evidence of the "saturation current" is observed.

Here it may also be mentioned that the $\eta - \lg i$ curves in alcoholic HCl solutions have the same character as in aqueous solutions, but lie 128 mV lower (see Fig. 4). As shown by Lewina and Silberfarb[2], on mercury the lowering under these conditions is of the same order, *viz.* 160 mV.

As to the dilute solutions, from 0.001 N and at higher dilutions the fact that the overvoltage is independent of concentration as observed in our experiments, is in itself no sufficient evidence for establishing the mechanism of overvoltage. The independence of the overvoltage on the pH is in agreement with the recombination mechanism. However, in this case, according to Okamoto, Horiuti and Hirota[7], a "saturation current" should be expected at 1×10^{-5} A/cm.^{2}, which, however, is not observed.

On the other hand, if there were an electrochemical mechanism, the independence of the overvoltage on concentration might be observed only in solutions of pure acids, while in the presence of a neutral salt excess the overvoltage should not remain invariable any longer, and with a tenfold dilution should increase by 58 mV,

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[6] S. Lewina and W. Sarinsky, Acta Physicochimica URSS, **7**, 485 (1937).

[7] G. Okamoto, I. Horiuti and K. Hirota, Sc. pap. Inst. Phys. Chem. Res., **29**, 223 (1936).

as was shown on the mercury cathode by Lewina and Sarinsky[6]. Our data on concentrations below 0.01 N do not support this conclusion. Unfortunately, in solutions with a dilution greater than 0.001 N, *i. e.*, in the region where the overvoltage is observed to be independent of the concentration in solutions of pure acids, it was not found possible to study the effect of salts; nor could the question of the "saturation current" be settled. Owing to the low electric conductivity of the solutions in this concentration range, the region of current densities studied was limited, and therefore it was not possible to reach the intersection point of the η — lg i curves for pure acid and for salt addition; nor could any measurements at high current densities be made where the appearance of "saturation current" could be expected.

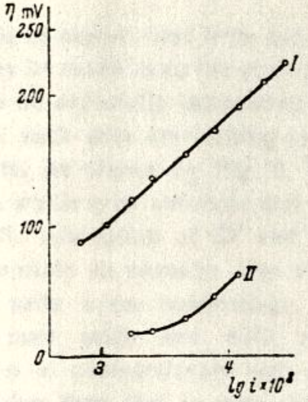

Fig. 4. *I* — 0.085 *N* HCl solution in water, *II* — 0.08 *N* HCl solution in alcohol.

Thus the question as to the overvoltage mechanism in the range of concentrations from 0.001 N and more dilute, remains as yet unsolved. It is contemplated to solve it by studying the kinetics of deuterium exchange on nickel in dilute solutions.

In conclusion, the question of the effect of different anions upon the overvoltage should be considered. As shown by Jofa,

Kabanov, Kuchinsky, Chistyakov[8], as well as by **Jofa**[9], in the case of the mercury cathode the adsorption of Cl′ and Br′ ions greatly lowers the value of overvoltage, especially in the region of small currents.

In normal solutions of HCl and HBr this effect is very strongly pronounced, and for HBr it is noticeable even in a 0.1 N solution.

Thus, it is natural to expect that from the course of the $\eta - \lg i$ curves conclusions may be made as to the capillary activity of different anions. This seems to be especially interesting with regard to nickel, since in the literature such data are lacking in view of the difficulty of direct measurements. As shown by Fig. 2, the curves in H_2SO_4, HCl and HBr coincide, which is an evidence that on nickel, as opposed to mercury, no specific adsorption of Cl′ and Br′ ions is observed. Here it will be appropriate to consider also the mechanism of the influence of neutral salts upon overvoltage. As noted above, the $\eta - \lg i$ curves in pure acids and with neutral salt addition intersect. In the region of comparatively high current density values the overvoltage is higher than that in pure acid, while in the region of small values it is lower. Such a fact could be explained by assuming that the point of zero surface charge on nickel corresponds to the intersection of curves in pure acid and with salt addition. The fact of the coincidence of these points (see Fig. 3) in H_2SO_4, HCl and HBr proves also the absence of specific adsorption of Cl′ and Br′ ions on nickel. The determination of the zero surface charge point on nickel from the $\eta - \lg i$ curves is of considerable interest in so far as direct measurements of this value are lacking[10].

It should be noted, however, that the determination of the point of zero surface charge at one concentration does not agree quite well with the data obtained at other concentrations. Thus, if for a 0.0015 N solution the potential of the zero surface charge is equal

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[8] S. Jofa, B. Kabanov, E. Kuchinsky and P. Chistyakow, Acta Physicochimica URSS, 10 317 (1939).

[9] S. Jofa, Acta Physicochimica URSS, 10, 903 (1939).

[10] The attempts of Möller (Z. physik. Chem. 65, 226, 1908) to determine it by measuring the contact angle value did not yield reliable results,

to $-0.163-0.118=-0.281$ V[11], then in the absence of specific adsorption for 0.012 N HCl the potential of the point of zero charge on nickel must also be equal to -0.281 V, *i. e.*, the curves in pure acid and in acid with salt addition must intersect at the overvoltage value of $-0.111-(-0.281)=0.170$ V[12]. In reality the intersection point lies at $\eta=0.143$ V. This discrepancy is not so very large, if we consider that the determination itself of the zero point from the intersection of curves in pure acid and with salt addition is insufficiently precise in some cases. However, this discrepancy becomes increasingly marked when passing to more concentrated solutions. Thus, already in 0.085 N HCl, the potential of the zero point from experimental data is found to be displaced by 90 mV to more positive values as compared to the value which is obtained if the intersection of curves in 0.001 N HCl is taken as the zero point. The causes of this discrepancy remain so far unexplained.

Summary

1. Hydrogen overvoltage has been measured on nickel in solutions of H_2SO_4, HCl and HBr within the range of concentrations from 1 N to 5×10^{-5} N and in the range of current densities from 1×10^{-8} to 1×10^{-2} A/cm.^{2}.

2. The initial portions of the $\eta - \lg i$ curves have a nearly horizontal course; in the range of higher current densities the curves follow Tafel's equation $\eta=a+b \lg i$ and retain a linear course within the whole range measured. No "saturation current" is observed.

3. For concentrations from 0.01 N to 1 N the correctness of the electrochemical mechanism of overvoltage, connected with the kinetics of the hydrogen ion discharge, has been confirmed. With more dilute solutions the overvoltage becomes independent of the concentration.

4. It is shown that the hydrogen overvoltage on nickel has closely approaching values in solutions of H_2SO_4, HCl and HBr.

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[11] 0.118 V — the value of overvoltage at the point of intersection of curves in pure acid and with addition of salt; —0,163 V — the potential of the hydrogen electrode in 0.0015 N HCl with respect to the normal hydrogen electrode.

[12] —0.111 V — the potential of the hydrogen electrode in 0.012 N HCl with respect to the normal hydrogen electrode.

Within the concentration range studied no specific adsorption of Cl′ and Br′ ions on nickel is observed.

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