Theory of the Discharge of Hydrogen Ions

II. Mercury. Concentrated Solution of Acids

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Experimental data[1]. With all the acids investigated at concentrations exceeding 0.1 *N* the overvoltage is no longer independent of the concentration and decreases as the latter increases. In the solutions investigated, except the most concentrated solu-

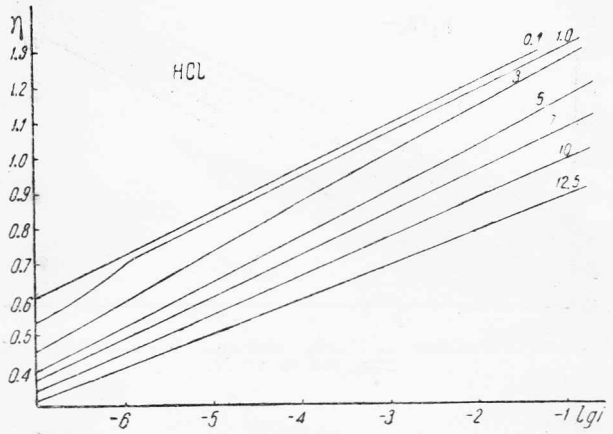

Fig. 1. Overvoltage in HCl solutions. Concentration range from 0.1 to 12.5 *N*.

tions of HCl, the decrease of η falls as i increases, but the law of change is different for different acids as it is seen from Figs. 1, 2, 3 and 4 in which the data for HCl, HBr, H_2SO_4, and $HClO_4$ are represented. The concentration of pure solutions of acids in this paper is expressed in g.-eq. per litre of solution.

In concentrated solutions of HBr as i increases the lowering of η first increases and then diminishes; it is possible that such

[1] J o f a, Acta Physicochimica URSS, **10**, 903 (1939). J. Phys. Chem. (Russ.), **13**, 1435 (1939) and Dissertation, University of Moscow, 1940.

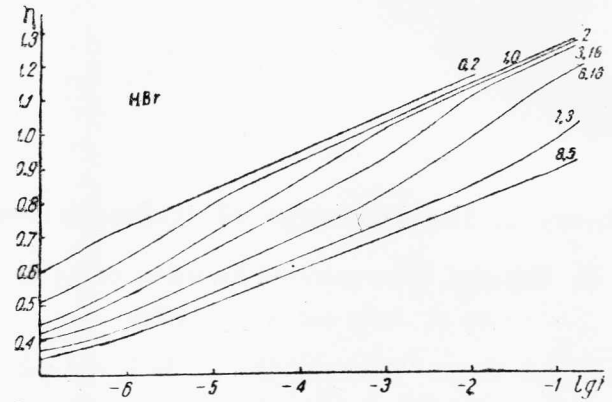

Fig. 2. Overvoltage in HBr solutions. Concentration range from 0.2 to 8.5 N.

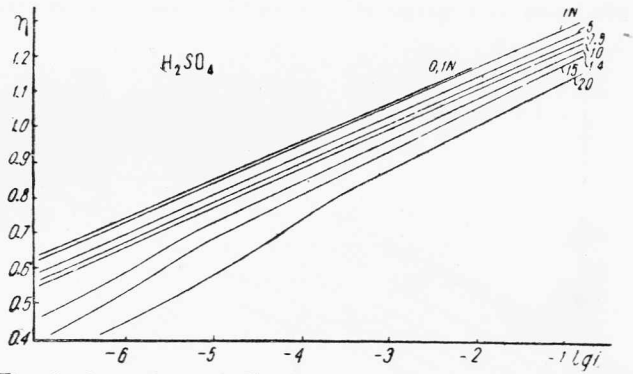

Fig. 3. Overvoltage in H_2SO_4 solutions. Concentration range from 0.1 to 20 N.

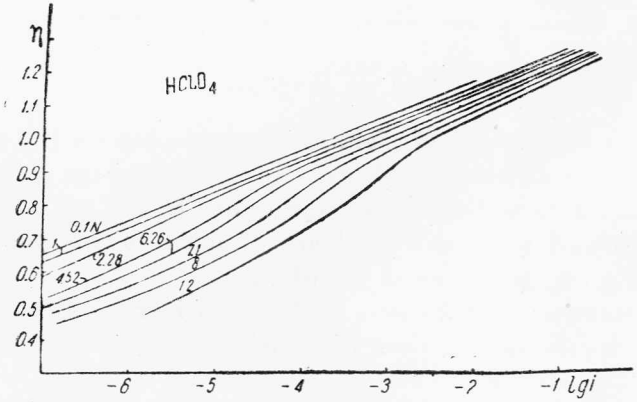

Fig. 4. Overvoltage in $HClO_4$ solutions. Concentration range from 0.1 to 12 N.

a relation would be also observed for HCl if it were possible to continue the measurements up to still higher current densities. The results of the measurements may also be represented, as it has been done by Jofa[2], in form of curves expressing the dependence of η upon the logarithm of the mean ionic activity of the acid $\lg a_{\pm}$ at constant current density. In the region of higher concentrations the value of η decreases almost linearly with the increase of $\lg a_{\pm}$.

The theory of hydrogen evolution from concentrated solutions of acids

The theory of the discharge of hydrogen ions in concentrated solutions offers great difficulties which at the present time cannot be completely overcome. In order to investigate the effect of various factors upon the electrochemical reaction, it is necessary to compare the current intensities at constant cathodic potential. However, we do not have the means to compare the potentials of electrodes in concentrated solutions of different concentrations. Therefore the following considerations are only of an approximate kind; but we hope that they still can be of help for the further development of the problem. Equations (10) and (10a) of the first paper of this series in the case of dilute solutions can be derived in the following way. The difference in the energy levels between the transition state of the reaction and a hydrogen ion in the solution is equal to

$$[\alpha(\varphi - \psi_1) + \psi_1] F + \text{const.} \tag{1}$$

It is supposed thereby that the hydrogen ions coming in contact with the metal are in equilibrium with the ions in the bulk of the solution and the potential at a distance of an ionic radius from the surface of the metal is designated by ψ_1. The physical meaning of the constant α may be explained in different ways. It follows from (1) that the rate of the discharge reaction is equal to

$$i = \text{const} \cdot [H^+] \, e^{-\frac{[\alpha(\varphi-\psi_1)+\psi_1]F}{RT}}, \tag{2}$$

whence equations (10) and (10a) are obtained. The above consideration can also be applied to concentrated solutions, however, in this

[2] Jofa, Acta Physicochimica URSS, **10**, 911 (1939).

case it is necessary to take into account the change in the character of the bond between the ion and the solvent, in the manner as it was done by Polanyi and Horiuti[3] when comparing the rate of the electrode process in various solvents.

Let us denote by f_H the activity coefficient of H^+ and by f_T the activity coefficient of the transition state. Then the corresponding correction in equation (1) can be expressed by means of the quantity

$$RT \ln f_T - RT \ln f_{H^+} = -(1-\lambda) RT \ln f_{H^+} = -\alpha' RT \ln f_{H^+},$$

where λ is equal to the ratio of the change of the free energy of solvation in the transition state to the change of the free energy of an ion in the bulk of the solution when going over to high concentrations, and $\alpha' = 1-\lambda$.

After introducing this correction, we obtain instead of equation (2)

$$i = \text{const} \cdot [H^+] f_{H^+}^{\alpha'} e^{-\frac{\alpha\varphi + (1-\alpha)\psi_1}{RT} F}$$

whence

$$\varphi = -\frac{1-\alpha}{\alpha}\psi_1 - \frac{RT}{\alpha F} \ln i + \frac{RT}{\alpha F} \ln [H^+] + \frac{\alpha'}{\alpha}\frac{RT}{F} \ln f_{H^+}, \qquad (3)$$

and

$$\eta = \frac{1-\alpha}{\alpha}\psi_1 + \frac{RT}{\alpha F} \ln i + \left(1 - \frac{1}{\alpha}\right)\frac{RT}{F} \ln [H^+] + \left(1 - \frac{\alpha'}{\alpha}\right)\frac{RT}{F} \ln f_{H^+}. \qquad (3a)$$

When $\alpha = \frac{1}{2}$, equation (3a) transforms into

$$\eta = \psi_1 + \frac{2RT}{F} \ln i - \frac{RT}{F} \ln [H^+] + (1-2\alpha')\frac{RT}{F} \ln f_{H^+}. \qquad (4)$$

The value of f_{H^+} cannot be determined directly from experiment. In the following instead of this quantity we shall make use of the quantity γ — the mean coefficient of activity of the ions of the acid — for an approximate comparison between the changes of activity and overvoltage.

It was pointed out above that at sufficiently high concentrations η changes linearly with $\ln a_\pm$. For this reason one may suppose that the last term of equation (4) has a decisive

[3] Horiuti and Polanyi, Acta Physicochimica URSS, **2**, 505 (1935).

influence upon η. However, this conclusion is incorrect since ψ_1 also changes linearly with a change of $\ln a_\pm$. This is shown by the measurement of electrocapillary curves carried out by Jofa, Ustinsky and Eiman[4]. The potential of the maximum of the electrocapillary curve $(\varphi_{max})_r$, referred to the reversible hydrogen electrode in the same solution, is equal to

$$(\varphi_{max})_r = \psi_1 - \varphi_H,$$

where φ_H is the value of the reversible hydrogen potential in the given solution. Hence

$$\psi_1 = (\varphi_{max})_r + \varphi_H = (\varphi_{max})_r + \frac{RT}{F} \ln a_{H^+} + \varphi_0, \qquad (5)$$

where φ_0 is the potential of a normal hydrogen electrode. The values of φ_H and φ_0 in equation (5), evidently, should be taken relatively to an electrode with a zero potential drop within the double layer, *i. e.* relatively to the electrocapillary maximum in dilute solutions of inactive electrolytes. Since the latter is situated at a potential ~ -0.50 referred to the normal calomel electrode $\varphi_0 \sim 0.22$. Instead of the quantity a_{H^+} in equation (5) we have to take the mean activity of ions of the acid $a_\pm$ and for H_2SO_4 the quantity $2^{1/3}a_\pm$; it is impossible to determine at the present moment to what extent such a substitution is permissible in concentrated solutions. In Fig. 5 the ordinates represent the quantity $(\varphi_{max})_r + \frac{RT}{F} \ln a_\pm + 0.22$ in the case of HCl and HBr and $(\varphi_{max})_r + \frac{RT}{F} \ln 2^{1/3}a_\pm + 0.22$ in the case of H_2SO_4 as depending upon $\lg a_\pm$[5]. As it may be seen at sufficiently high concentrations a linear relation is observed within the limits of accuracy of the determination of $(\varphi_{max})_r$ which was not very great. In dilute solutions the quantity ψ_1, according to its definition, approaches asymptotically zero [6].

[4] Jofa, Ustinsky and Eiman, J. Phys. Chem. (Russ.), **13**, 934 (1939).

[5] The activities were calculated according to Lewis and Randall and using also data of Jonny, J. Amer. Chem. Soc., **50**, 989 (1928) and of Harned and Hammett, J. Amer. Chem. Soc., **57**, 27 (1935); $a_\pm = \gamma m$ for HCl and HBr and $a_\pm = 2^{2/3}\gamma m$ for H_2SO_4, where m is the concentration in moles per 1000 g. H_2O.

[6] Essin and Markov [J. Phys. Chem. (Russ.), **13**, 318 (1939)] were the first to demonstrate on the example of Kl the existence of a logarithmic relation between the potential of the maximum of the electrocapillary curve and the activity of the electrolyte.

The existence of a logarithmic relation between ψ_1 and the activity suggests that the potential drop in these solutions in the maximum of the electrocapillary curve is caused by orientated dipoles of the acid, between which there exist sufficient repulsive forces. The value of the dipole moment increases in the sequence $HBr < HCl < H_2SO_4$.

Another circumstance which leads us to suppose that the main factor, determining the decrease of the overvoltage in

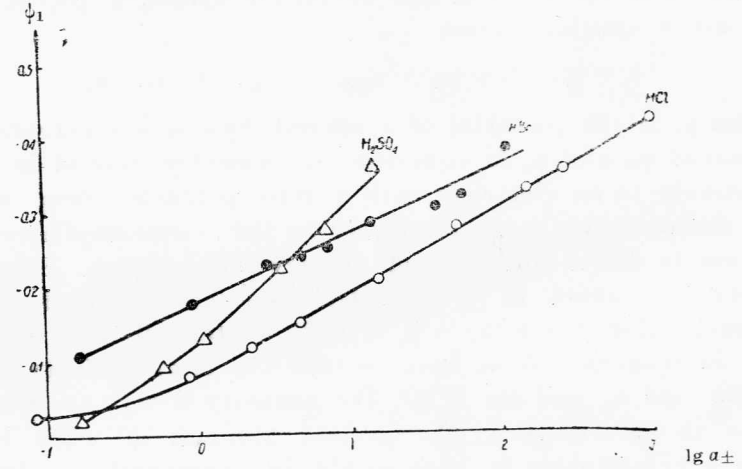

Fig. 5. The relation between the adsorption potential ψ_1 and the activity of ions in concentrated solutions of acids.

concentrated solutions, must be the change in the composition of the surface layer and not the change in the activity coefficient of the acid, is the dependence of this decrease upon the potential. In all the solutions so far investigated, except HCl at the highest concentrations, this decrease is diminished when the current density increases. For some systems as, for instance, particularly for $HClO_4$, the decrease of η which is still observed at the highest current densities can be completely explained by the term $-\frac{RT}{F}\ln[H^+]$ in equation (4). The dependence of the overvoltage decrease on the potential can hardly be explained in any other way than by connecting this decrease with the presence of anions in the double layer. These anions are desorbed when the potential becomes sufficiently negative. Jofa[7] made

[7] Jofa, Acta Physicochimica URSS, **10**, 908 (1939).

an attempt to establish a quantitative relation between the magnitude of the decrease of η at different potentials and the concentration of an ion, for instance, of Cl′ in the surface layer $[Cl']_s$, computed according to the equation

$$[Cl']_s = \Gamma_{Cl'} + d \times 10^{-3}c, \qquad (6)$$

where $\Gamma_{Cl'}$ is the value of the anion adsorption found from electrocapillary data with the aid of the Gibbs equation and d — the thickness of the surface layer assumed to be equal to 3.1×10^{-8}. In a certain range of current densities and concentrations it follows from the above comparison that the decrease of η is observed at such potentials at which we are to suppose, on the basis of equation (6), the presence of anions in the surface layer of the cathode. However, the investigation of a wider range of concentrations and potentials and also of the behaviour of $HClO_4$ and H_2SO_4 solutions convinces us that equation (6) cannot be considered as a sound basis for such a calculation. Thus, in $HClO_4$ solutions even at the highest concentrations (12N) at sufficiently negative potentials the decrease of η almost vanishes, while equation (6) at such a high bulk concentration always gives a positive value for the surface concentration. It seems necessary to take into account that the presence of anions by itself does not lead to the appearance of a negative adsorption potential in the surface layer, if it is not accompanied by a definite orientation of ionic pairs composed by a cation and an anion.

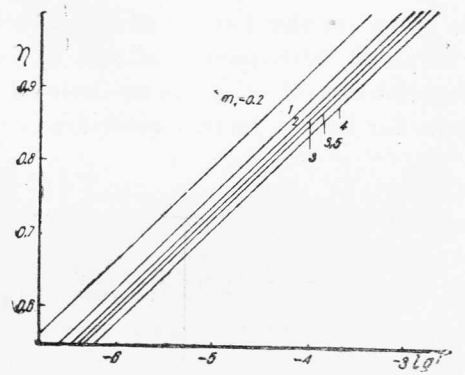

Fig. 6. Overvoltage in solutions of m_1HCl+ $+(4-m_1)$ KCl in 1000 g. H_2O.

In determining the influence of the activity of ions on overvoltage the measurements of η in m_1 HCl + m_2 KCl and m_1 HCl + $+ m_2$ Li Cl at constant anion concentration are of special interest. The results of these measurements for the first system are given in Fig. 6; m_1 and m_2 are the concentrations of HCl and of KCl or respectively LiCl in moles per 1000 g. of water. In these

experiments the sum $m_1+m_2=4$ was kept constant. At a constant concentration of the anion the quantity ψ_1 probably remains almost constant and the change of η according to equation (4) should be connected with the change of $[H^+]$ and $\ln f_{H^+}$. The latter quantity in both systems changes in a different manner: in solutions containing KCl it is noticeably smaller than in pure HCl, while the substitution of Li^+ for H^+ has almost no influence on the activity coefficient of HCl. Results of these measurements are given in Table 1. In the second column the variation of the quantity $\frac{RT}{F}\ln[H^+]$ or more exactly $\frac{RT}{F}\ln m_1$ is given; in the third and the fourth columns the increase of η as compared with pure acid and in the fifth and sixth columns the logarithms of the mean activity coefficient of H^+ and Cl^- ions for both systems according to Hawkins[8].

Table 1

m_1	$-\frac{RT}{F}\Delta\ln m_1$	$\Delta\eta$ HCl+KCl $i=10^{-4}$	$\Delta\eta$ HCl+LiCl $i=10^{-4}$	lg γ HCl+KCl	lg γ HCl+LiCl
4	—	—	—	0.244	0.244
3.5	0.003	0.011	0.008	—	—
3	0.007	0.021	0.015	0.171	0.250
2	0.017	0.031	0.025	0.104	0.262
1	0.035	0.047	0.044	0.042	0.261
0.2	0.075	0.086	0.086	—0.010	0.262

It is seen from the table that the changes of η in both cases almost coincide inspite of a considerable difference in the activity coefficients of the acid; the complete coincidence of the quantities $\Delta\eta$ in the presence of a great excess of salt, when the difference in the activities is the largest, is especially remarkable. The quantities $\Delta\eta$ are close to $-\frac{RT}{F}\Delta\ln m_1$ although for small additions of the salt the increase of η is greater than $-\frac{RT}{F}\Delta\ln m_1$. The reason for the latter effect is not clear. The

[8] Hawkins, J. Amer. Chem. Soc., **54**, 4480 (1932).

data in Table 1 show that the term $(1-2\alpha')\frac{RT}{F}\ln f_{H^+}$ in equation (4) cannot have a direct influence upon the quantity η, or, in other words, that α' is close to 0.5 Apparently, there exists the same relation between the change of the energy level of the transition state and the total change of the free energy of solvation as in the case of the change of the electric potential. However, the experimental material on the basis of which this conclusion is drawn should be enlarged.

If we admit that $\alpha'=0{,}5$ then equation (4) is simplified, since the term with $\ln f_{H^+}$ disappears. As it has already been pointed out, ψ_1 can be determined from equation (5) for every concentration if the potential corresponds to the maximum of the electrocapillary curve. However, it is possible to measure the current intensity at this potential only for more concentrated solutions, since at lower concentrations the current in the maximum of the electrocapillary curve is too small. With HBr solutions the current at this potential could be measured for concentrations equal to $2N$ and above. In this case ψ_1 can be compared with the decrease of overvoltage with respect to the value that would be obtained at the same current intensity if $\psi_1=0$. The latter may be found from the overvoltage curve for

Table 2

HBr

C	ψ_1	$\Delta\eta+\Delta\frac{PT}{F}\ln[H^+]$	C	ψ_1	$\Delta\eta+\Delta\frac{RT}{F}\ln[H^+]$
$2N$	−0.22	−0.12	$5.16N$	−0.32	−0.18
$3.16N$	−0.25	−0.13	$7.3N$	−0.38	−0.25

the $1N$ solution by extrapolating for lower current densities the rectilinear part of the curve, which is not influenced by the adsorption of anions and is expressed according to Jofa by the equation $\eta=1.411+0.119\ \lg i$. We designate with $\Delta\eta$ the difference between the value of η found experimentally for a solution of a given concentration and the value calculated

in this way. In Table 2 the values of $\Delta\eta + \Delta \frac{RT}{F} \ln [H^+]$ and of ψ_1 for HBr solutions[9] are compared.

According to equation (4), ψ_1 and $\Delta\eta + \Delta \frac{RT}{F} \ln [H^+]$ should be equal; actually, as far as absolute values are concerned, the latter expression is considerably smaller than ψ_1. This divergence can be diminished if in computing ψ_1 we take f_{H^+} not equal to γ as it was done in the present paper, but greater than it. Such a supposition was made in a paper of Jofa[10] and as it may be seen from equation (4) it leads to a lowering of the calculated value of $|\psi_1|$. However, as it was shown by Jofa no reasonable supposition as to the relation between f_{H^+} and γ can account for this disagreement. Similar results are obtained with other acids. Consequently, in this case also we come to the conclusion that the picture of the double layer which we used here is too rough for a quantitative calculation of the influence of the ion adsorption upon overvoltage, although it is suitable for a correct qualitative description. A closer approximation to experiment could be obtained if one were to suppose, as it is done by Whitney and Grahame[11] that the anion centres approach considerably closer the surface of the mercury than the cation centres.

Summary

1. The decrease of overvoltage observed in concentrated solutions of acids is determined by the change in the structure of the boundary layer and by the increase of the concentration of the H^+ ions. The activity coefficent enters into the expression for the rate of discharge in such a way that it does not influence the value of overvoltage in any considerable extent.

2. In HCl +KCl and HCl +LiCl solutions, at equal concentrations, the values of overvoltage are close to each other in spite of the difference in the activity coefficients of the acids.

3. There exists a linear relation between the value of the adsorption potential ψ_1 found from the measurements of the electrocapillary curves in concentrated solutions of acids and the logarithm of the mean activity coefficient of the acid.

4. The decrease of overvoltage in concentrated solutions of acids observed experimentally is smaller than the value calculated from the corresponding change of the ψ_1 potential.

[9] The values of the mean coefficients of activity for the computation of ψ_1 with the aid of equation (5) were taken from Livingston, J. Amer. Chem. Soc., **48**, 45 (1926) and Harned, ibid., **51**, 416 (1929); $[H^+]$ was taken equal to the volume concentration.

[10] Jofa, J. Phys. Chem. (Russ)., **13**, 1443 (1939).

[11] Whitney and Grahame, J. Chem. Phys., **9**, 827 (1941).

Note added in proof. The linear relation between ψ_1 and $a_\pm$ holds also for $HClO_4$ solutions. In this case $\psi_1 = 0.055 + 0.104 \lg a_\pm$ in the interval $0.3 < \lg a_\pm < 2.5$.

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