

The Overvoltage on a Mercury Cathode in Concentrated Solutions of Acids.

I. Hydrochloric and hydrobromic acids

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The problem of the dependence of the overvoltage upon the concentration in solutions of acids has been repeatedly examined in the literature¹. However, the experimental material hitherto obtained refers to acid concentrations not higher than 2 N and fails to afford an exhaustive solution of this problem.

We will not give here an account of the material which refers to dilute solutions, since it is examined in detail in two papers by Lewina and Sarinsky². We shall only mention that in these papers the equation derived by A. Frumkin³ was confirmed:

$$\varphi + \psi_1 = \frac{2RT}{F} \ln [H^+] - \frac{2RT}{F} \ln i + \text{const.}, \quad (1)$$

where φ is the potential of the cathode, ψ_1 — the value of the potential at a distance of one ionic radius from the surface of the metal, $[H^+]$ the concentration of hydrogen ions in the solution, and the current density⁴. In the presence of an excess of a neutral salt, the increase in the concentration of hydrogen ions in the solution

¹ I. Tafel, Z. physik. Chem., **50**, 641 (1905). Glasston, J. Am. Chem. Soc., **46**, 2646 (1924). F. Bowden, Trans. Farad. Soc., **24**, 473 (1928). F. Bowden, Proc. Roy. Soc., **126**, 107 (1929). P. Herasymenko, Rec. Trav. Chem. Pays-Bas, **44**, 503 (1925). P. Herasymenko a. Slendyk, Z. physik. Chem., **A 149**, 123 (1930).

² S. Lewina a. W. Sarinsky, Acta Physicochimica URSS, **6**, 481 (1937). S. Lewina a. W. Sarinsky, Acta Physicochimica URSS, **8**, 493 (1937).

³ A. Frumkin, Z. physik. Chem., **A 164**, 121 (1933).

⁴ According to Stern's theory, in dilute solutions the quantity ψ_1 may be identified with the electro-kinetic potential (ζ -potential):

produces only an insignificant effect on the value of the ψ_1 -potential, and then, at $i = \text{const.}$, we have:

$$\varphi = \frac{2RT}{F} \ln [H^+] + \text{const.} \quad (2)$$

and

$$\eta = -\frac{RT}{F} \ln [H^+] + \text{const.},$$

where η is the overvoltage.

However, in the absence of a neutral salt the following relation holds for a dilute solution of acid:

$$\psi_1 = \frac{RT}{F} \ln [H^+] + \text{const.} \quad (3)$$

Substituting equation (3) into equation (1) we find that

$$\eta = \text{const.}$$

Here the constancy of the overvoltage with a change in concentration is a result of the change in the structure of the double layer and is only true when certain conditions are observed under which equation (3) retains its validity.

In this lies the essential difference between the theory of the retarded discharge of ions and the theory of recombination according to which, at least as a first approximation, the overvoltage under all conditions does not depend upon the composition of the solution⁵.

According to the theory of retarded discharge the conclusion that the overvoltage is independent of the hydrogen ion concentration in solution applies to dilute solutions only. In more concentrated solutions of acids, in the absence of specific adsorption, the quantity ψ_1 in equation (1) may be disregarded, and under these conditions the overvoltage with a ten-fold increase in the concentration, should be decreased by 0.058 V., just as in the presence of an excess of a neutral salt.

However, upon a closer examination of this question, it is easy to notice that new factors appear in the case of concentrated solutions of acids. As follows from investigations of the hydrogen overvoltage in solutions of surface active electrolytes⁶, one of these

⁵ A. Frumkin, *Acta Physicochimica URSS*, **7**, 475 (1937).

⁶ S. Jofa, B. Kabanov, E. Kuchinski and F. Chistyakov, *Acta Physicochimica URSS*, **10**, 317 (1939).

factors is a change in the structure of the double layer and in the value of the ψ_1 -potential, which is caused by the specific adsorption of anions.

Another factor is the change in the hydration equilibrium of hydrogen ions in solution which is reflected in an increase in the activity coefficient of the acid. Both of these factors must undoubtedly affect the rate of discharge of the hydrogen ions, and, consequently, the magnitude of the overvoltage also.

Experimental part

The measurements of the overvoltage were carried out on a large mercury cathode making use of a method which was described in detail in a preceding paper⁷. In order to maintain the temperature constant, the apparatus employed in the present investigation was placed into a thermostat which was kept at $20 \pm 0.2^\circ \text{C}$. In Figs. 1 and 2 curves are presented for solutions of hydrochloric and hydrobromic acids showing the dependence of the overvoltage on the logarithm of the current density.

From the curves presented in these figures it is evident in the first place that the overvoltage markedly decreases with an increase in the concentration of the acid.

At low concentrations (0.1 *N* HCl and 0.2 *N* HBr) the dependence of η upon $\lg i$ is represented by a straight line with a slope $b = 0.118 - 0.12 \text{ V.}$, which is in agreement with Volmer's theory and the experimental data of Bowden and Rideal⁷, Lewina and Sarinsky², and other investigators⁸.

With an increase in the concentration, the shape of the curves departs from linearity. At the same time the general slope of the curves also changes. For 1 *N* hydrochloric acid there appears a region of reduced values of the overvoltage for small values of the current density; at $i = 1.2 \times 10^{-6}$ the curve passes into a straight line with a slope equal to 0.119 V.

For 3 *N* acid, this transition spreads out over almost the entire curve, which leads to an increased slope equal to 0.140 V. in the

⁷ F. Bowden and E. Rideal, *Proc. Roy. Soc.*, **120**, 59 (1928).

⁸ S. Lewina and M. Silberfarb, *Acta Physicochimica URSS*, **4**, 275 (1936). B. Kabanov, *Acta Physicochimica URSS*, **5**, 193 (1936).

middle portion of the curve. For 5 *N* acid, though the dependence of η upon $\lg i$ is represented by a straight line, the presence of some additional decrease in the overvoltage at small and medium values of the current density is still noticeable. This is expressed by a slight increase in the slope of the straight line ($b=0.124$ V.) in comparison with the slope both for the lower and the higher concentrations (10 and 12.5 *N*) for which the slope of the curve again decreases markedly ($b=0.106$ and 0.093 V.).

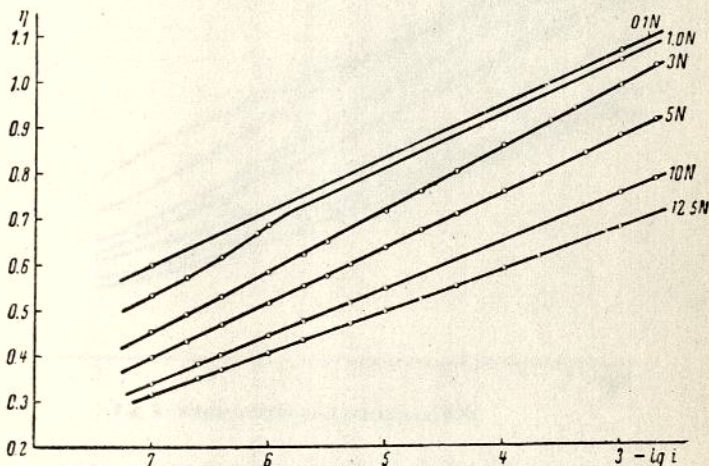


Fig. 1. Relation between η and $\lg i$ for HCl.

The decrease in the overvoltage with an increase in the concentration is still more sharply expressed in the case of hydrobromic acid. The anomalies in the shape of the curves are more pronounced in this case than in the case of HCl⁹. The region of decreased values of the overvoltage for HBr already becomes noticeable on the curve for 0.2 *N* HBr at $i=7.5 \times 10^{-7}$ A/cm.², while for 1 *N* HBr this region extends to $i=10^{-5}$, and for 2 *N* HBr, to 7×10^{-4} A/cm.². Even for 3 and 5 *N* HBr, at high values of the current density one can still notice a tendency of the curve to change its course when approaching higher values of the overvoltage.

⁹ Similar results were obtained by A. N. Kolychev for HBr by employing a dropping mercury electrode.

For concentrated solutions of HBr the points expressing the overvoltage at small values of $\lg i$ lie higher than the linear continuation of the middle part of the curve. This, apparently, is connected with the appearance of Hg ions at the electrode owing to the reaction of the Hg with the acid. This effect is connected with

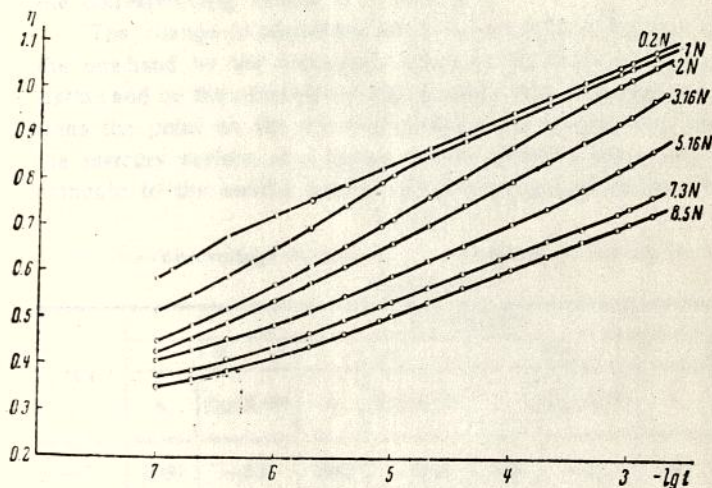


Fig. 2. Relation between η and $\lg i$ for HBr.

the great stability of the complex anions formed. This is indicated by the fact that, at these values of the potential, in concentrated solutions of HBr the mobility of the mercury in the capillary ceases while measurements are being carried out with a capillary electrometer to obtain the electrocapillary curve.

Discussion

The above-mentioned anomalies in the shape of the curves may be explained on the basis of measurements of the overvoltage in solutions of surface active electrolytes⁶. According to these measurements, the decrease in the overvoltage at small current densities is connected with the adsorption of the anion. In order to apply these ideas the surface concentration of the anion must be calculated for the solutions investigated for different potentials. Such a cal-

culatation may be made from the electrocapillary curves with the aid of the Gibbs adsorption formula¹⁰.

As an example, in Table 1 values are presented for the adsorption of the anion, $\Gamma_{Cl'}$, in the case of hydrochloric acid, calculated from the electrocapillary curves for various concentrations, and also the corresponding values of η and $\lg i$.

The change in adsorption with concentration is determined here on the one hand by the immediate effect of the increase in the concentration and on the other by the circumstance that at increased concentrations the point on the electrocapillary curve representing the state of the mercury surface at a given current density passes over from the cathodic to the anodic branch owing to a decrease in the overvoltage.

Table 1

η —overvoltage in mV., $\Gamma_{Cl'}$ —adsorption of the Cl' -ion in mols/cm.²

$\lg i$	Concentration							
	1 N		3 N		5 N		10 N	
	η	$\Gamma_{Cl'} \times 10^{10}$	η	$\Gamma_{Cl'} \times 10^{10}$	η	$\Gamma_{Cl'} \times 10^{10}$	η	$\Gamma_{Cl'} \times 10^{10}$
-3	1060	-0.7	1000	-0.89	890	-1.1	760	-0.3
-4	940	-0.5	863	-0.82	770	-0.8	660	0.1
-5	820	-0.46	730	-0.73	645	-0.35	555	0.7
-6	690	-0.41	590	-0.4	520	0.18	450	1.1
-6.5	605	-0.28	522	-0.19	460	0.65	395	1.4
-7	535	-0.15	460	-0.08	397	1.2	340	1.6

The values obtained for $\Gamma_{Cl'}$ denote adsorption, while in order to take into account the effect of the chlorine ion, its surface concentration $[Cl']_s$, must be known. Since there is no theory which would determine to what depth the change in concentration extends near the surface in these systems, we cannot carry out such a calculation exactly. If we suppose that the whole adsorption effect is localized within a layer of one molecule of water, *i. e.*, 3.1×10^{-8} cm. thick, then

$$[Cl']_s = \Gamma_{Cl'} + 3.1 \times 10^{-8} \times 10^{-3} c, \quad (4)$$

where c is the HCl concentration in moles per litre.

¹⁰ S. Jofa a. A. Frumkin, Acta Physicochimica URSS, 10, 473 (1939).

When $\Gamma_{Cl'}$ is negative, such a calculation, of course, gives only a lower limit of $[Cl']$. This follows also from the fact that this computation for small concentrations leads to negative values which have no direct physical meaning. However, the value of $[Cl']$ in these cases is undoubtedly small, and we conventionally assume it to be equal to zero.

Table 2 contains the values of $[Cl']$, for potentials which correspond to current densities whose negative logarithms are equal to 3, 4, 5, 6, 6.5, and 7, respectively, for all the concentrations studied.

Table 2 obtained in this manner leads to an interesting conclusion. For the concentrations 10 and 12.5 *N* at all the current densities studied, we have a considerable concentration of ions in the surface layer which does not change very much with a change of potential (1:1.66 for 10 *N* and 1:1.4 for 12.5 *N*); but for 5 *N* HCl $[Cl']$ varies already within wide limits (1:6.1). For $c=3$,

at high current densities the value of $[Cl']$ is quite small and sharply increases (1:21) with a decrease in the current density. In conformance with this, for the 3 and 5 *N* acid, when the current density is decreased, the slope of the $\eta - \lg i$ curve increases. For 1 *N* HCl, the estimation of $[Cl']$ by our method gives a negative value which at a current density lower than 10^{-6} A/cm.² becomes positive. A marked increase of $[Cl']$ at $i=10^{-6}$ leads to the appearance of an inflexion on the $\eta - \lg i$ curve.

In the communication which will appear in Russian¹¹ a similar calculation is included for the surface concentration of the anion for hydrobromic acid. The change of $[Br']$ with the current density for

Table 2
Values of $[Cl']$,

$\lg i$	Concentration <i>c</i>				
	1 <i>N</i>	3 <i>N</i>	5 <i>N</i>	10 <i>N</i>	12.5 <i>N</i>
3	—	0.04	0.45	2.8	(3.9)*
4	—	0.11	0.95	3.2	(4.2)
5	—	0.20	1.2	3.8	(4.6)
6	—	0.53	1.73	4.2	(5.0)
6.5	0.03	0.74	2.2	4.5	(5.3)
7	0.16	0.85	2.75	4.7	(5.5)

* The values for 12.5 *N* acid were obtained by extrapolation.

¹¹ S. Jofa, J. Phys. Chem. (Russ.), in print.

various acid concentrations affords a possibility of explaining the anomalies in the shape of the curves for this acid as well.

It is also of interest to compare the overvoltage curves for various acids at those concentrations for which the specific adsorption effect may be neglected. This comparison is especially interesting, since in the preceding communication⁶ we showed how considerably the measurements of the overvoltage on mercury, published recently by other investigators, differ both from each other and from ours. From an examination of Fig. 4 of the paper just mentioned⁶, it is seen that the values of the overvoltage obtained with 0.1 N HCl and 1.0 N H₂SO₄ nearly coincide. The overvoltage curve obtained with 0.2 N HBr is also very close to the two curves.

Upon examination of the curves presented in Figs. 1 and 2, one may draw the conclusion that the appearance of an anion in the surface layer is probably not the only factor which causes a decrease in the overvoltage. This follows most readily from a comparison of the values of η for large acid concentrations. In this case the adsorption of the anion changes but little, but the dependence of the overvoltage upon the concentration remains on the whole the same as in the case of lower concentrations. This may be illustrated by the fact that the dependence of the overvoltage upon $\lg a_{\pm}$, where $a_{\pm}$ is the mean activity of the ions of the acid, is represented at low current densities sufficiently well by a straight line. At higher current densities and low concentrations a disturbing effect due to the penetration of the anion into the double layer is observed, as follows from what has been stated above (see Fig. 3: the dependence of η upon $\lg a_{\pm}$ for HCl at various current densities).

A theoretical investigation of the dependence of the overvoltage upon the activity or upon the acid concentration unfortunately encounters considerable difficulties, since a comparison of the rate of ionic discharge must be carried out not at constant overvoltage but at constant surface potentials. This, strictly speaking, is impossible to carry out in concentrated solutions in which nothing is known about the individual activity coefficients of the ions.

One may still attempt to give an equation (for details see the communication in Russian) which will represent the influence on the overvoltage both of the changes in the structure of the double layer

connected with the penetration of the anion into it, and of the change in the properties of the volume phase.

With $i = \text{const.}$ and $\alpha = 1/2$, this equation has the following form:

$$\eta - \psi_1 = -\frac{RT}{F} \ln [H^+] + \frac{2RT}{F} \beta' (1 - 2\alpha') \ln f_{a\pm} + \text{const.}, \quad (5)$$

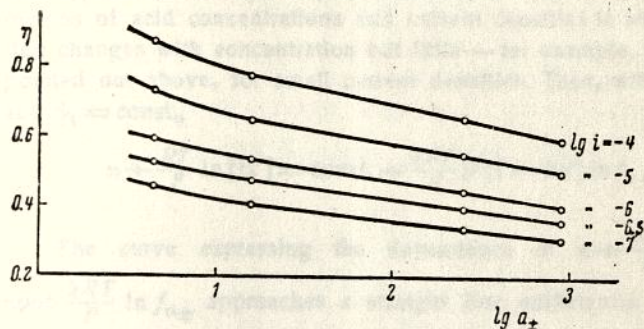


Fig. 3. Relation between η and $\lg a_{\pm}$ for HCl.

where α has the meaning usually assigned to it in the theory of overvoltage; β' is the ratio of the logarithm of the activity coefficient of the hydrogen ion to $2 \ln f_{a\pm}$ (i. e., it is a coefficient expressing the fraction of the anomaly of the activity coefficient which must be ascribed to the hydrogen ion); and α' is the ratio of the change in the energy of activation of the electrode process to the change in the free energy of solvation.

This equation may be applied without using the term containing $\ln f_{a\pm}$, i. e., setting $\alpha' = 1/2$; then the equation will assume the form

$$\eta - \psi_1 = -\frac{RT}{F} \ln [H^+] + \text{const.} \quad (6)$$

If ψ_1 is determined from the shift of the maximum of the electrocapillary curves for overvoltage values which are not too far from electrocapillary maximum of the given solution, then the dependence of the overvoltage upon the concentration qualitatively agrees with this equation. For the purpose of obtaining a quantitative agreement with experiment for both acids studied an empirical coefficient approximately equal to 0.6—0.8 must be introduced into this equation before ψ_1 .

This result confirms the connection between the change in overvoltage and the value of ψ_1 , which was found previously during an investigation of the overvoltage in acidified solutions of surface active salts.

To take into account the effect of the activity coefficient of the acid, ψ_1 in equation (5) may be assumed to be a constant for those regions of acid concentrations and current densities in which adsorption changes with concentration but little—for example, as has been pointed out above, for small current densities. Then, with $i = \text{const.}$ and $\psi_1 = \text{const.}$,

$$\eta + \frac{RT}{F} \ln [H^+] = \text{const.} + \frac{2RT}{F} \beta' (1 - 2\alpha') \ln f_{a\pm}. \quad (7)$$

The curve expressing the dependence of $\eta + \frac{RT}{F} \ln [H^+]$ upon $\frac{2RT}{F} \ln f_{a\pm}$ approaches a straight line sufficiently well if the current density is small, but the computation of the constant α' from the experimental data for HCl according to this equation, even if β' is taken as equal to unity, gives a value which is too high—namely 0.78.

Evidently, the effect of the specific adsorption of the anion is still superimposed in this case upon the influence of the activity coefficient of the acid.

A complete quantitative solution of the problem here examined will be made possible only after the conditions will be found which will permit separating both factors involved.

In very concentrated acid solutions, moreover, the possible discharge of the acid molecules present in the double layer may be superimposed upon the effects already discussed. The decrease in the slope of the $\eta - \lg i$ curve at very high acid concentrations points, apparently, to this.

In conclusion it is my pleasant duty to express my deep gratitude to Prof. A. Frumkin for his valuable advice which was of great help in the execution of this investigation.

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